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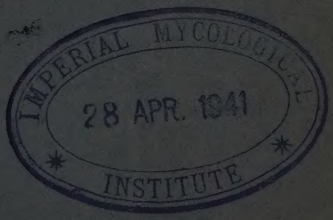


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*MATHÉMATIQUES*

# SUR UN CRITÉRIUM D'IRRÉDUCTIBILITÉ DE POLYNÔMES

Par M. V. JAKOVKIN

*(Présenté par A. N. Kolmogoroff, de l'Académie, le 4. VII. 1940)*

Commençons par énoncer un théorème sans en donner une démonstration.

Théorème. *Toute fonction rationnelle $f(x)$, définie dans le corps des nombres réels, peut être transformée, par une substitution de la forme $x=y+h$, en une fonction $F(y)$ telle que tous ses coefficients sont du même signe que celui du terme principal et que chacun de ses multiplicateurs, dans ce corps, ne contient que les coefficients du même signe.*

La démonstration de ce théorème est analogue à celle d'un lemme connu de M. Mandl (1). Faisons observer seulement que, pour tout $h$ réel non inférieur à la borne supérieure des parties réelles des racines de $f(x)$, le théorème en question a toujours lieu.

En faisant usage de ce théorème nous allons démontrer le critérium suivant de l'irréductibilité de polynômes dans le corps des nombres rationnels.

Théorème. *Soit*

$$f(x)=a_0x^n+a_1x^{n-1}+\ldots+a_n$$

*un polynôme aux coefficients entiers et soit $R$ la borne supérieure des parties réelles des racines de ce polynôme. S'il existe deux nombres rationnels $\frac{p_1}{q_1}$ et $\frac{p_2}{q_2}$ dont l'un est positif et l'autre n'est pas inférieur à $R$ tels que*

$$\left[\frac{q_1q_2}{(q_1,\ q_2)}\right]^n f\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)$$

*est un nombre premier, alors le polynôme $f(x)$ est irréductible dans le corps des nombres rationnels.*

Démonstration. Supposons le contraire, c'est-à-dire supposons que le polynôme $f(x)$ soit réductible. Nous pouvons alors écrire:

$$f(x)=\varphi(x)\cdot\psi(x) \qquad (1)$$

où $\varphi(x)=b_0x^r+b_1x^{r-1}+\ldots+b_r$ et $\psi(x)=c_0x^s+c_1x^{s-1}+\ldots+c_s$ sont des polynômes aux coefficients entiers.

Sans restreindre la généralité, nous pouvons supposer $\frac{p_2}{q_2}\geqslant R$ et $\frac{p_1}{q_1}>0$.

En substituant dans les deux membres de l'égalité (1) $x=y+\frac{p_2}{q_2}$, nous obtenons

$$f\left(y+\frac{p_2}{q_2}\right)=\varphi\left(y+\frac{p_2}{q_2}\right)\psi\left(y+\frac{p_2}{q_2}\right). \qquad (2)$$

Or, $\frac{p_2}{q_2}\geqslant R$, donc d'après le théorème précédent les fonctions

$$f\left(y+\frac{p_2}{q_2}\right),\quad \varphi\left(y+\frac{p_2}{q_2}\right)\quad \text{et}\quad \psi\left(y+\frac{p_2}{q_2}\right)$$

contiennent les coefficients d'un même signe seulement. De plus, chacune d'elles contient deux termes aux moins, puisque le terme de degré nul de la fonction $f\left(y+\frac{p_2}{q_2}\right)$ est différent de zéro.

Substituons maintenant dans l'égalité (2) au lieu de $y$ le nombre positif rationnel $\frac{p_1}{q_1}$; cela nous donne

$$f\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)=\varphi\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)\psi\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right). \qquad (3)$$

Chacun des nombres

$$f\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right),\quad \varphi\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)\quad \text{et}\quad \psi\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)$$

est une somme de deux termes au moins. Tous les termes de ces expressions sont des fractions rationnelles du même signe que leurs dénominateurs, qui sont des produits de puissances entières des nombres $q_1$ et $q_2$.

Multiplions les deux membres de l'égalité (3) par le plus petit multiple des plus grandes puissances de $q_1$ et $q_2$ se trouvant aux dénominateurs, c'est-à-dire par

$$\left[\frac{q_1q_2}{(q_1;\ q_2)}\right]^n=\left[\frac{q_1q_2}{(q_1;\ q_2)}\right]^r\cdot\left[\frac{q_1q_2}{(q_1;\ q_2)}\right]^s.$$

Alors nous aurons

$$\left[\frac{q_1q_2}{(q_1;\ q_2)}\right]^n f\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)=\left[\frac{q_1q_2}{(q_1;\ q_2)}\right]^r\varphi\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)\left[\frac{q_1q_2}{(q_1;\ q_2)}\right]^s\psi\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)$$

où

$$\left[\frac{q_1q_2}{(q_1;\ q_2)}\right]^r\varphi\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)\quad\text{et}\quad\left[\frac{q_1q_2}{q_1;\ q_2}\right]^s\psi\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)$$

sont des sommes, contenant deux termes au moins de nombres entiers d'un même signe. Donc, chacune de ces expressions est un entier différent de 0 et de $\pm 1$.

Ainsi nous voyons que l'hypothèse de la réductibilité du polynôme $f(x)$ nous a conduit à la conclusion que le nombre

$$\left[\frac{q_1q_2}{(q_1;\ q_2)}\right]^n f\left(\frac{p_1}{q_1}+\frac{p_2}{q_2}\right)$$

est représentable comme produit de deux entiers différents de 0 et de $\pm 1$; ce nombre est donc composé, tandis que nous l'avons supposé premier.

Il résulte, comme cas particulier, de ce théorème un corollaire analogue au critérium connu d'irréductibilité que l'on doit à G. Polya [2] (pour $q_1 = q_2 = p_1 = 1$ et $p_2 = k$).

De plus, pour les polynômes $f(x)$ aux coefficients entiers positifs inférieurs à 10, il résulte du théorème énoncé le critérium bien connu de A. Cohn [2].

Considérons un exemple. Soit:

$$f(x) = x^4 - 2x^3 - 2x^2 - 2x - 1.$$

On peut prendre $R = 3$, puisque

$$\frac{A}{|a_0|} + 1 = \frac{2}{1} + 1$$

et puisque le nombre

$$3^4 f\left(\frac{10}{3}\right) = 3^4 f\left(\frac{1}{3} + 3\right) = 1579$$

est un nombre premier; le polynôme $f(x)$ est irréductible dans le corps des nombres rationnels.

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LITTÉRATURE CITÉE

[1] M. Mandl, ZS. f. reine und angew. Math., 113, 252 (1894). [2] Polya und Szegö, Aufgaben und Lehrsätze aus der Analysis, II.

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*MATHÉMATIQUES*

# L'ANAMORPHOSE DES POLYNÔMES

Par P. V. NIKOLAEV

*(Présenté par A. N. Kolmogoroff, de l'Académie, le 6. VII. 1940)*

I. Les matrices de l'anamorphose des polynômes de Masseau. Supposons que le polynôme $F(t_1, t_2, t_3)$ soit représenté sous la forme

$$F(t_1, t_2, t_3) \equiv \sum_{i=0}^{m_{k+1}} \sum_{j=0}^{m_{k+2}} t_{k+1}^i t_{k+2}^j V_{ij}^{(k)} \qquad (1)$$

d'un polynôme de variables $t_{k+1}$, $t_{k+2}$ aux coefficients appartenant à l'anneau $J^{(k)}$ des polynômes en $t_k$ ($k=1, 2, 3$; et pour $k+l>3$, $t_{k+l}^i \equiv t_{k+l-3}^i$).

Appellons matrice d'ordre $k$ de l'anamorphose ou, tout court, $A$-matrice d'ordre $k$ du polynôme (1), la matrice $T^{(k)} = \| V_{ij}^{(k)} \|$ considérée comme tableau à double entrée:

| $T^{(k)}$ | $t_{k+2}^0$ | . . | $t_{k+2}^{m_{k+2}}$ |
|---|---|---|---|
| $t_{k+1}^0$ | $V_{00}^{(k)}$ | . . | $V_{0,\, m_{k+2}}^{(k)}$ |
| . | . | . . | . |
| . | . | . . | . |
| $t_{k+1}^{m_{k+1}}$ | $V_{m_{k+1},\, 0}^{(k)}$ | . . | $V_{m_{k+1},\, m_{k+2}}^{(k)}$ |

(2)

Choisissons pour $t_{k+l}$ ($l=1, 2$) un système d'un certain nombre de polynômes:

$$R_{k+l};\ R_{k+l,\,0}^{(k)},\ R_{k+l,\,i}^{(k)},\ \ldots,\ R_{k+l,\,\overline{m}_{k+l}}^{(k)} \quad [\text{pour } k+l>3,\ R_{k+l} \equiv R_{k+l-3}] \qquad (3)$$

aux coefficients tirés de l'anneau $J^{(k)}$, de façon à satisfaire aux trois conditions suivantes:

a) $R_{k+l,\,0}^{(k)}, \ldots, R_{k+l,\,\overline{m}_{k+l}}^{(k)}$ sont des polynômes de degrés non supérieurs à $m_{k+l}$, l'ordre du polynôme $F(t_1, t_2, t_3)$ relativement à la variable $t_{k+l}$.

b) Les éléments de chacun des systèmes $(R_{k+l})$, $(l=1, 2)$, doivent être linéairement indépendants relativement à l'anneau $J^{(k)}$, c'est-à-dire que de l'identité $\sum_{i=0}^{\overline{m}_{k+l}} f_i(t_k)\, R_{k+l,\,i}^{(k)} \equiv 0$ résulte toujours $f_i(t_k) \equiv 0$ $(i=0, \ldots, \overline{m}_{k+l})$.

c) Il existe une matrice $\overline{T}^{(k)} = \| \overline{V}_{ij}^{(k)} \|$ formée d'éléments appartenants à l'anneau $J^{(k)}$, contenant $1 + \overline{m}_{k+1}$ lignes et $1 + \overline{m}_{k+2}$ colonnes, telle que pour le polynôme donné $F(t_1, t_2, t_3)$ a lieu l'identité

$$F(t_1, t_2, t_3) \equiv \sum_{i=0}^{\overline{m}_{k+1}} \sum_{j=0}^{\overline{m}_{k+2}} R_{k+1,\,i}^{(k)} R_{k+2,\,j}^{(k)} \overline{V}_{ij}^{(k)} . \qquad (4)$$

La matrice $\overline{T}^{(k)} = \| \overline{V}_{ij}^{(k)} \|$ sera appelée $A$-matrice partielle d'ordre $k$ du polynôme $F(t_1, t_2, t_3)$; les systèmes $(R_{k+1})$ et $(R_{k+2})$ seront appelés, respectivement, premier et second système générateurs de cette matrice.

Le rang $\overline{\delta}_k$, les facteurs invariants $\overline{E}_0^{(k)}, \overline{E}_2^{(k)}, \ldots, \overline{E}_{\overline{\delta}_k}^{(k)}$ de la $A$-matrice partielle d'ordre $k$ $\overline{T}^{(k)}$ du polynôme $F(t_1, t_2, t_3)$ dont les systèmes générateurs sont formés des polynômes indépendants de $t_k$, satisfont aux égalités:

$$\overline{\delta}_k = \delta_k \qquad (5)$$

$$\overline{E}_i^{(k)} = \overline{E}_i^{(k)} \quad (i = 1, 2, \ldots, \delta_k) \qquad (6)$$

où $\overline{\delta}_k$ est le rang de la $A$-matrice d'ordre $k$ $\overline{T}^{(k)}$ du polynôme $F(t_1, t_2, t_3)$ et $E_1^{(k)}, \ldots, E_{\delta_k}^{(k)}$ sont ses facteurs invariants.

Admettons que dans l'anamorphose $A$

$$F(t_1, t_2, t_3) \equiv | f_{k1}\, f_{k2}\, f_{k3} | \qquad (7)$$

celles des fonctions du système

$$(R_{k+1})\, f_{k+1,1},\ f_{k+1,2},\ f_{k+1,3}$$

qui sont différentes de zéro, soient linéairement indépendantes et qu'il en est de même pour celles des fonctions du système

$$(R_{k+2})\, f_{k+2,1},\ f_{k+2,2},\ f_{k+2,3}$$

qui ne sont pas nulles.

Les systèmes $(R_{k+1})$ et $(R_{k+2})$ sont les systèmes générateurs de la $A$-matrice partielle d'ordre $k$ du polynôme $F(t_1, t_2, t_3)$. Nous appellerons cette matrice — matrice de Masseau d'ordre $k$ du polynôme $F(t_1, t_2, t_3)$, correspondant à l'anamorphose $A$, ou bien, tout court, sa $M$-matrice d'ordre $k$.

En tenant compte du genre du polynôme par rapport à chacune des variables $t_{k+1}$, $t_{k+2}$, on peut prendre pour la $M$-matrice d'ordre $k$ du polynôme donné l'une des matrices suivantes:

| $M^{(k)}$ | $f_{k+2,1}$ | $f_{k+2,2}$ | $f_{k+2,3}$ |
|---|---|---|---|
| $f_{k+1,1}$ | 0 | $f_{k3}$ | $-f_{k2}$ |
| $f_{k+1,2}$ | $-f_{k3}$ | 0 | $f_{k1}$ |
| $f_{k+1,3}$ | $f_{k2}$ | $-f_{k1}$ | 0 |

(8)

| $M^{(k)}$ | $f_{k+2,1}$ | $f_{k+2,3}$ |
|---|---|---|
| $f_{k+1,1}$ | 0 | $-f_{k2}$ |
| $f_{k+1,2}$ | $-f_{k3}$ | $f_{k1}$ |
| $f_{k+1,3}$ | $f_{k2}$ | 0 |
| | $(f_{k+2,2} = 0)$ | |

(8′)

| $M^{(k)}$ | $f_{k+2,1}$ | $f_{k+2,2}$ | $f_{k+2,3}$ |
|---|---|---|---|
| $f_{k+1,2}$ | $-f_{k3}$ | 0 | $f_{k1}$ |
| $f_{k+1,3}$ | $f_{k2}$ | $-f_{k1}$ | 0 |
| | $(f_{k+1,1} = 0)$ | | |

(8″)

| $M^{(k)}$ | $f_{k+2,1}$ | $f_{k+2,3}$ |
|---|---|---|
| $f_{k+1,2}$ | $-f_{k3}$ | $f_{k1}$ |
| $f_{k+1,3}$ | $f_{k2}$ | 0 |
| | $(f_{k+1,1} = 0;\ f_{k+2,2} = 0)$ | |

(8‴)

Le rang de chacune de ces matrices est égal à 2; par conséquent, le rang $\delta_k$ de chacune des $A$-matrices $T^{(k)}$ du polynôme de Masseau est, lui aussi, égal à 2.

Pour les $A$-matrices des polynômes réduits, les premiers facteurs invariants sont égaux à 1.

Dans ce travail nous déterminons les seconds facteurs invariants des $A$-matrices de polynômes normaux; en particulier, pour les polynômes du genre 3 ils sont aussi égaux à 1.

II. L'anamorphose des polynômes. Ordonnons le polynôme $F(t_1, t_2, t_3)$ d'ordre $m_k$, relativement à $t_k$, suivant les puissances de l'une des variables, $t_1$ par exemple:

$$t_1^{m_1}\varphi_{10}^{(23)} + t_1^{m_1-1}\varphi_{11}^{(23)} + \ldots + \varphi_{1m_1}^{(23)} \equiv F(t_1, t_2, t_3) \tag{9}$$

$$[\text{où } \varphi_{ij}^{(23)} \equiv \varphi_{ij}(t_2, t_3)].$$

Nous pouvons extraire de la suite de polynômes

$$\varphi_{10}^{(23)},\ \varphi_{11}^{(23)},\ \ldots,\ \varphi_{1m_1}^{(23)} \tag{10}$$

une sous-suite

$$F_{11}^{(23)},\ F_{12}^{(23)},\ \ldots,\ F_{1r_1}^{(23)}\ \ [F_{1i}^{(23)} \equiv F_{1i}(t_2, t_3)] \tag{11}$$

de la façon suivante: $F_{11}^{(23)} \equiv \varphi_{10}^{(23)}$ et $F_{1i}^{(23)}$ est le premier des termes de la suite (10) linéairement indépendant des $i-1$ termes précédents, déja définis, de la sous-suite (11). Le polynôme $F(t_1, t_2, t_3)$ peut être représenté sous la forme

$$F(t_1, t_2, t_3) \equiv \sum_{i=1}^{r_1} f_{1i} F_{1i}^{(23)} \tag{12}$$

où $f_{1i} \equiv f_{1i}(t_1)$ sont des polynômes de la variable $t_1$. Appellons premier développement canonique du polynôme $F(t_1, t_2, t_3)$ sa représentation sous la forme (12); les polynômes $F_{1i}^{(23)}$ seront appelés coefficients du développement et le système des polynômes $f_{1i}$ portera le nom du système générateur du développement considéré.

Le $k$-ième développement canonique du polynôme de Masseau contient deux termes ($r_k = 2$) si et seulement si ce polynôme est de genre nul relativement à la variable $t_k$.

Parmi les $A$-matrices partielles $\overline{T}^{(k)}$ du polynôme $F(t_1, t_2, t_3)$ pour tout $k$ ($k = 1, 2, 3$) se trouve une matrice, dont les systèmes générateurs sont des systèmes générateurs des développements canoniques correspondants du polynôme $F(t_1, t_2, t_3)$. Les éléments de cette matrice sont des combinaisons linéaires des éléments du système générateur du $k$-ième développement canonique. Appellons cette matrice $A$-matrice canonique.

Pour les polynômes de Masseau la $A$-matrice canonique $\overline{T}^{(k)}$ est équivalente à la $M^{(k)}$-matrice de Masseau.

Si l'on suppose que le nombre des colonnes de la matrice $M^{(k)}$ est non inférieur au nombre de ses lignes, alors la matrice $M^{(k)}$ peut avoir l'une des formes suivantes:

$$M_1^{(k)} = \begin{Vmatrix} 0 & f_{k3} & -f_{k2} \\ -f_{k3} & 0 & f_{k1} \\ f_{k2} & -f_{k1} & 0 \end{Vmatrix}; \tag{13}$$

$$M_2^{(k)} = \begin{Vmatrix} -f_{k3} & 0 & f_{k1} \\ f_{k2} & -f_{k1} & 0 \end{Vmatrix}; \quad (13') \qquad M_3^{(k)} = \begin{Vmatrix} -f_{k3} & f_{k1} \\ f_{k2} & 0 \end{Vmatrix} \qquad (13'')$$

où $f_{ki}$ sont des polynômes de la variable $t_k$.

Pour qu'un polynôme $F(t_1, t_2, t_3)$, possédant un facteur irréductible de toutes les trois variables, admette une anamorphose rationnelle, il est nécessaire que, pour $k$ quelconque ($k=1, 2, 3$), la $A$-matrice canonique $\overline{T}^{(k)}$ dont le nombre de colonnes n'est pas inférieur au nombre de lignes, satisfasse aux conditions suivantes:

1. Si $\overline{T}^{(k)}$ a deux colonnes, il existe deux constantes $\alpha$ et $\beta$ telles que le produit $P \cdot \overline{T}^{(k)} \cdot Q$, où

$$P = \begin{Vmatrix} 1 & 0 \\ -\alpha & 1 \end{Vmatrix}; \qquad Q = \begin{Vmatrix} 1 & -\beta \\ 0 & 1 \end{Vmatrix} \qquad (14)$$

fournit une matrice de rang deux, l'un des éléments de laquelle est nul, c'est-à-dire, à une permutation de lignes (de colonnes) près, ce produit donne

$$M_3^{(k)}. \qquad (13'')$$

2. Si $\overline{T}^{(k)}$ a trois colonnes, il existe une matrice non singulière $C$ aux elements constants telle que

$$\overline{T}^{(k)} C = M^{(k)}$$

où $M^{(k)}$ est une matrice de l'une des formes (13) ou (13'); et il est suffisant que l'une de ces conditions ait lieu pour une valeur quelconque de $k$.

Les conditions formulées permettent non seulement de répondre à la question, si un polynôme donné admet ou non une anamorphose rationnelle, mais de plus elles indiquent un algorithme pour la recherche de l'anamorphose au cas de polynômes de Masseau.

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*ASTRONOMY*

# RESULTS OF OBSERVATIONS OF THE CORONA SPECTRUM JUNE 19, 1936 AT OMSK

By G. SHAJN, Member of the Academy

A report of the results of this work was read at the Meeting of the Solar Commission at Pulkovo in January 1939. The paper itself was presented more than a year ago, but owing to a delay in publication, a summary of the results of spectrophotometric study of corona spectrum obtained at the eclipse of June 19, 1936 at Omsk is given now in this periodical. The dispersion used is 35.8 Å per mm at Hγ. A series of spectra of the sun and lamp has been obtained for calibration and comparison, using the same spectrograph with a step-slit.

The method of measurements is as follows. For many portions of each of the 11 lines measured and for adjacent portions of the continuous spectrum at various distances from the moon's limb a series of microphotometric tracings has been obtained (Fig. 1). This permits to compute the full intensity or

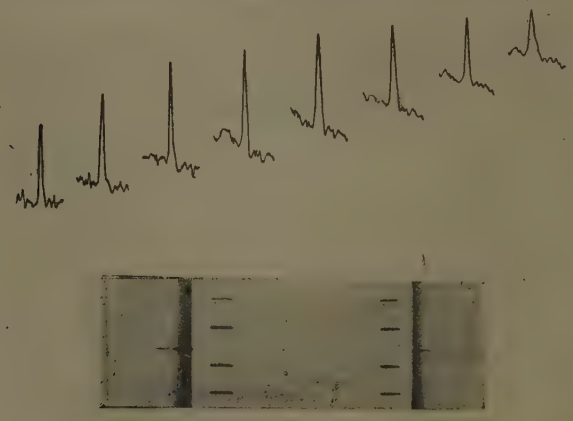

Fig. 1. Microphotometric tracings of coronal line 5303. Below is the spectrum of corona near the line 5303.

equivalent width $\int J\,d\lambda$ in the units of intensity of the continuous spectrum (Angström units).

One of the main results is that the intensity of emission lines changes within large limits absolutely and relatively when passing from one region

of the corona to another and from one eclipse to another. The comparison of intensities of emission coronal lines as well as of their ratios in the eclipse 1929 (Grotrian in Sumatra) and 1936 (Omsk) (it is during these two eclipses that the spectrophotometric method was first applied to emission lines) brings out very considerable differences. For instance, in 1936 the equivalent width in the above units is 18.3 and 9.4 for the lines 5303 and 6374 respectively, while in 1929 the width for the same lines is 27.5 and 2.0, the accuracy being about 20%. The same holds for the lines in the violet region (in 1929 the line 3801 is very faint, not measurable, and 3987 fainter than 4086, while in 1936 the line 3987 is sensibly brighter than 4086, and 3801 is sufficiently intense). On our spectrogram a considerable difference in the intensity of emission lines may be also noted when comparing the measured intensities of emission lines of east and west sides of the corona. As compared with earlier suggestions and observations in this respect (prismatic camera observations and especially those made without eclipse by Lyot) we have here a proof based on the spectrophotometric measurements. In addition, it is shown that, when passing from one point of corona to another and from one eclipse to another, the intensity of emission lines changes not only absolutely and relatively, but even when expressed in the units of intensity of neighbouring continuous spectrum. The fact of such a large variation of absolute and relative values of intensities of emission lines is of importance for the interpretation of the corona.

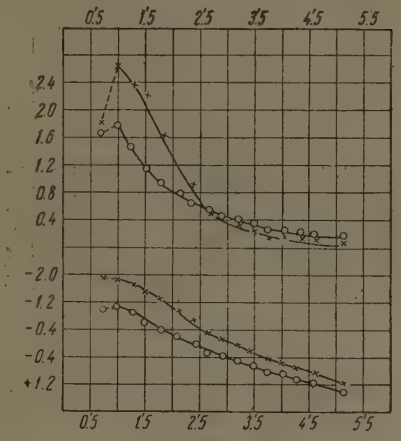


Fig. 2. Top. The change of full intensity of emission line 3987 (crosses) and of the continuous background (circles) as a function of the distance from the limb. The point of intersection of both curves is selected arbitrarily. Bottom. The change of sum of central intensity of line and of continuous background (crosses) and of continuous background alone (circles). The difference in the ordinates between two curves is so adjusted here to correspond to the observed difference (continuous background minus central intensity) for the distance about 1'.6.

In harmony with this behaviour of coronal emission lines is another important fact. Namely, no proportionality is observed between the fall of equivalent width of emission lines and the intensity of continuous spectrum with increasing distance from the solar limb, the intensity gradient for the former being much larger. This holds for all the lines (Fig. 2), except may be 4231. It is in disagreement with the result of Grotrian ([1]), who claimed the proportionality in question with all the important consequences of this statement. In our paper this point is discussed in details.

The deviation from proportionality between the intensity of emission lines and that of continuous spectrum with increasing distance from the limb and in general with changing brightness of different regions of corona, is obviously of high importance from the point of view of interaction between the matter responsible for the emission lines (atoms or ions) and that responsible for the continuous spectrum (free electrons).

The observed irregularities in the curves representing the changes [with the increasing distance from the limb] of the intensity of the emission lines and of the continuous background are to be ascribed primarily to the local effect.

Attention is paid to the difference in the relative intensity gradient of emission lines as a criterion for dividing the coronal lines in groups. In this respect the line 4231 is especially distinguishable. The change in the intensity of continuous background as a function of the distance within 1'—6' from the limb does not seem to be sensibly dependent on the wavelength.

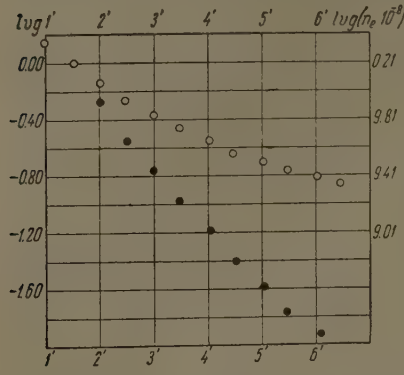


Fig. 3. The change of density as a function of the distance from the limb. Circles and dots relate to the matter responsible for the continuous background and emission lines. Ordinates to the left are log of relative values of the density of dots. Ordinates to the right are log of number of electrons per cm³.

A passage was made from the observed intensity $J(\rho)$ for the emission lines and continuous spectrum as a function of the distance from the limb to $F(r)$ and $D(r)$, expressing the radiation per unit volume and the density of matter in space at distance $r$ from the centre of sun. The function $F(r)$ is connected with the observed value $J(\rho)$ by

$$J(\rho) = \int_{-\infty}^{+\infty} F(r)\, dz.$$

The solution of this Abel's integral equation is known to give

$$F(r) = -\frac{1}{\pi} \int_{r}^{\infty} \frac{J'(\rho)\, d\rho}{\sqrt{\rho^2 - r^2}}.$$

The function $D(r)$ is simply proportional to $F(r)$ for the radiating particles (atoms); as to the reflecting or scattering particles (free electrons), the dependence of $D(r)$ on $F(r)$ is much more complicated. The main result is that while the density of matter responsible for the continuous spectrum (electrons) decreases within 1'.5—5'.5 nearly from $1.6 \times 10^8$ to $0.26 \times 10^8$ per cm³, the corresponding decrease for the atoms or ions responsible for the emission lines is nearly nine times more rapid (Fig. 3).

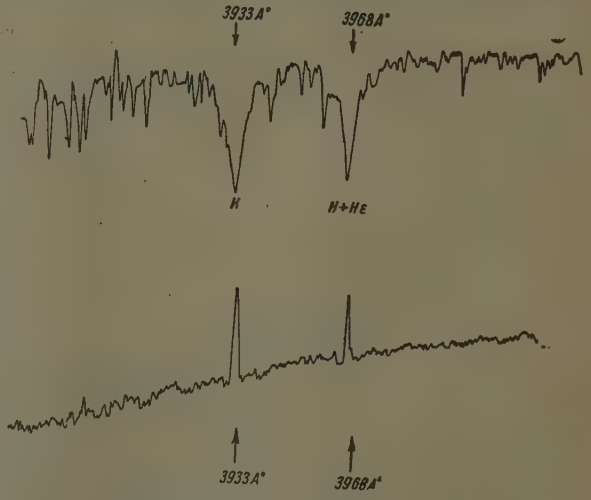


Fig. 4. Microphotometric tracing of the spectrum of sun (above) and of corona (below) in the region of lines K and H.

The serious departure from the proportionality under consideration is interpreted in the terms of ionization theory, and a suggestion has been made with respect to the ionization stage of atoms in the inner corona, if the presence of free electrons is really governed there by the usual processes.

The reality of the observed delay or even decrease in the intensity of emission lines with the approach to the limb from a distance of about 1' is doubtful. A decrease in the intensity at a distance less than 0'.5 from the limb may be suggested only on the basis of indirect considerations, mainly from the comparison of intensities of coronal and chromospheric lines.

The wave-lengths of coronal emission lines 3801, 3987, 4086, 4231 and 4567 have been measured, and for the two last lines large corrections to the table values were found.

A careful study of the spectrum of corona in the region 3850—4050 shows in opposition to Grotrian's[2] suggestion no trace of absorption lines of ionized calcium K and H (Fig. 4). A comparison with the computed theoretical profil leads to a striking discrepancy, and this seems to be experimentum crucis of the current theory of absorption lines in the spectrum of inner corona, which are supposed to be due to Doppler's broadening under the influence of thermal velocities of electrons. This is discussed from the point of view of reconciliation with the hypothesis of non-thermal motion of electrons, and some suggestions are made with respect to the effect of fast electrons.

There is an analogy between the coronal and some chromospheric lines (helium, hydrogen) with respect to their variability, their relationships to the continuous background and perhaps with respect to the delay in the intensity increase with approach to the solar limb (the last holds probably for helium in chromosphere). Basing on this and the known relationship between the protuberances and the details of coronal structure, as well as on the consideration of the motions and the conditions of excitation, one may assume that a single source (energetic emission of the ultra-violet quanta or of the fast particles) controls the equilibrium, motion and excitation in the chromosphere, in the protuberances and in the inner corona.

Crimea, Simeiz, Astronomical Observatory.

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9. VII. 1940.

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*HYDROTECHNIK*

# ÜBER DIE STABILITÄT DER VERKLEIDUNGSPLATTEN IN EINEM WASSERSTROM

Von J. D. GORODROW

*(Vorgelegt von N. E. Kotchin, Mitglied der Akademie, den 10. VI. 1940)*

Die Stabilität der Verkleidungsplatten in einem Wasserstrom ist mit einer grosser Menge verschiedener Fragen verbunden; wir beschränken uns auf das Studium der Einwirkung eines Stromes von unbegrenzter Breite auf rechteckige Verkleidungsplatten, die mit unbedeutenden Schlitzen auf die Sohle streng in einer und derselben Ebene aufgelegt sind, wobei die Strömung als eine ständige und gleichmässige vorausgesetzt wird.

Eine Erklärung der Ursachen der Ausspornung von sorgfältig gelegten Platten durch den Strom, wenn dieselben keiner frontalen Einwirkung ausgesetzt sind, ist nur durch die Eigenschaften eines turbulenten Stromes möglich, und zwar durch die Druckpulsationen, da in dem betrachteten Falle keine aufwärts gerichtete beständige Hubkraft vorhanden ist.

Dank den Fugen zwischen den Platten dringt das Wasser in die unterliegende Schicht ein; infolgedessen werden die Platten auf ihrer unteren Oberfläche einem Druck unterzogen, welcher als beständiger und dem hydrostatischen gleicher angenommen werden kann, da das Wasser unter den Platten fast unbeweglich ist. Auf die Oberfläche der Platten wirkt dagegen (ausser dem gemittelten hydrostatischen Drucke) ein nach Grösse und Vorzeichen veränderlicher Druck. Die Ausspornung der Platte aus dem Lager findet in dem Falle statt, wenn die Amplitude des pulsierenden Druckes genügend gross ist.

Amplitude des pulsierenden Druckes. Die Geschwindigkeitsverteilung in einem turbulenten Strome nach der Tiefe hängt nicht von der Einwirkungsart der äusseren Oberflächen auf den Strom ab: ob der letztere sich geschwind längs glatten oder langsam längs rauhen Wandungen bewegt, ist die Stromstruktur die gleiche, wenn in den beiden Fällen die Kraft der Wandreibung (1) eine gleiche ist. Diese Eigenschaft des turbulenten Stromes führt dazu, dass die Änderung der Durchflussmenge bei einer entsprechenden Rauhigkeitsänderung (einer derartigen, bei der aber sich das hydraulische Gefälle nicht ändert) lediglich eine parallelle Verschiebung der Geschwindigkeitskurve hervorruft; dasselbe wird auch durch die Versuche von Dönch, Nikuradze u. a. Forschern bestätigt. Einen analytischen Ausdruck der betrachteten Eigenschaft stellt die folgende Formel der Geschwindigkeitsverteilung für den Fall eines Stromes von unbegrenzter Breite dar:

$$v - v_0 = \sqrt{\frac{\tau_0}{\rho}}\, f\left(\frac{y}{H}\right). \qquad (1)$$

Hier sind: $v$ — die Geschwindigkeit im Abstande $y$ von der Sohle, $H$ — die Stromtiefe, $\tau_0$ — die auf die Flächeneinheit bezogene Reibung an der Sohlenoberfläche, $\rho$ — die Dichte der Flüssigkeit, $v_0$ — irgendeine besondere, z. B. die Oberflächen-, Mittel- oder Sohlengeschwindigkeit (die letztere an der Grenze der laminären Schicht). Der Bestimmtheit wegen werden wir unter $v_0$ die Sohlengeschwindigkeit verstehen.

Die Geschwindigkeitskurve wird durch drei Parameter $H$, $\frac{\tau_0}{\rho}$ und $v_0$ bestimmt. Die Änderung des Parameters $v_0$ ruft eine parallelle Verschiebung der genannten Kurve hervor, d. h. die Translationsgeschwindigkeit wird in jedem Punkte des Stromes sich um einen gleichen Wert verändern, was keine zusätzlichen Beschleunigungen herbeiführt und folglich die Kinematik der Wirbeln, die den Strom sättigen, nicht beeinträchtigt. Somit wird die kinematische Stromstruktur bloss durch zwei Parameter $H$ und $\frac{\tau_0}{\rho}$ bestimmt. Der zweite dieser Parameter $\frac{\tau_0}{\rho}$ kann durch die Differenz zwischen zwei irgendwelchen für die Strömung charakteristischen Geschwindigkeiten ausgedrückt werden, z. B. durch die Differenz zwischen den Oberflächen- und Sohlen- oder der Mittel- und Sohlengeschwindigkeiten. In der Tat, erhält man aus dem Ausdruck (1):

$$\sqrt{\frac{\tau_0}{\rho}} = \frac{1}{f(1)} \cdot (v_n - v_0) = A_1 \cdot (v_n - v_0) \qquad (2)$$

wo $v_n$ die Oberflächengeschwindigkeit ist, $A_1 = \frac{1}{f(1)} = \text{const.}$

Durch Integration von (1) wird

$$\sqrt{\frac{\tau_0}{\rho}} = \frac{1}{\int_0^{y=H} f\left(\frac{y}{H}\right) d\left(\frac{y}{H}\right)} (v_{mt} - v_0) = A_2 (v_{mt} - v_0) \qquad (3)$$

worin $v_{mt}$ die Mittelgeschwindigkeit längs der Lotrechten ist, $A_2 = \text{const.}$ Für die dynamische Schilderung des Stromes muss noch die Flüssigkeitsdichte $\rho$ angegeben sein.

Somit werden die Kinematik und die Dynamik, so wie auch folglich die Amplitude des pulsierenden Druckes durch drei Parameter bestimmt: 1) die Tiefe $H$, 2) die Differenz der Geschwindigkeiten $v_n - v_0$ oder $v_{mt} - v_0$, und 3) die Dichte $\rho$. Analytisch kann dasselbe in der Gestalt von

$$P_0 = f(H, \rho, v_{mt} - v_0) \qquad (4)$$

ausgedrückt werden.

Auf Grund des $\pi$-Theorems der Dimensionierungsanalyse (2) fällt es nicht schwer zu beweisen, dass die Beziehung (4) sich nur in einer einzigen völlig bestimmten Form gestalten kann und zwar

$$P_0 = k\rho (v_{mt} - v_0)^2 \qquad (5)$$

worin $k = \text{const.}$

Im Ausdruck (5) ist die Stromtiefe nicht enthalten, was auf folgende Weise erklärt werden kann: tiefe Ströme sind durch Wirbel von grossen Massen, aber von geringen Winkelgeschwindigkeiten gesättigt, seichte Ströme dagegen durch Wirbel von grossen Winkelgeschwindigkeiten, aber von geringen Massen, infolgedessen die zentrifugen Kräfte in den Wirbeln und folglich auch die Druckamplituden für beide Fälle gleich bleiben.

Nach Formel (5) folgt ebenfalls, dass die Amplitude des pulsierenden Druckes auf die Sohlenoberfläche nicht unmittelbar von der Mittelgeschwindigkeit, sondern von dem Überschuss der Mittelgeschwindigkeit im Vergleich zu der Sohlengeschwindigkeit abhängt. Dies wird dadurch erklärt, dass die Stromstruktur durch das parallelle Verschieben der Geschwindigkeitskurve nicht geändert wird. Der Unterschied in der Einwirkung auf die Sohlenoberfläche der Ströme mit gleichen relativen Geschwindigkeiten $v_{mt}-v_0$, aber mit verschiedenen absoluten Geschwindigkeiten $v_{mt}$, besteht nicht in der Amplitudengrösse des pulsierenden Druckes, sondern nur in der Grösse der Pulsationsperiode.

Es fällt nicht schwer die Amplitude $P_0$ nicht durch die Differenz $v_{mt}-v_0$, sondern durch die mittlere Geschwindigkeit $v_{mt}$ und den Koeffizient $C$ in der Formel von Chézy oder durch das hydraulische Gefälle auszudrücken. Mit Rücksicht auf die Beziehung

$$\tau_0 = \gamma i H \tag{6}$$

und die Formel von Chézy erhält man aus dem Ausdruck (3)

$$v_{mt} - v_0 = \frac{1}{A_2}\sqrt{giH}. \tag{7}$$

Nach der Substitution von (7) in die Formel (5) wird

$$P_0 = a\gamma Hi = a\gamma \frac{v_{mt}^2}{C^2} \tag{8}$$

worin $a = \frac{k}{A_2^2} = \text{const.}$

Der Ausdruck (8) zeigt, dass die Amplitude des pulsierenden Druckes gerade proportionell der treibenden Kraft ist.

K i p p m o m e n t. Die Ausspornung der Platten aus den ihnen entsprechenden Lagern geschieht unter der Einwirkung des durch den pulsierenden Druck verursachten Kippmoments. Für die Bestimmung dieses Momentes nehmen wir als erste Näherung die Verteilung des pulsierenden Druckes auf die Sohlenoberfläche als sinusoidale an:

$$P = P_0 \cos 2\pi \left(\frac{x}{\lambda} - \frac{t}{T}\right) \tag{9}$$

worin $P_0$ — die Amplitude des pulsierenden Druckes, $\lambda$ — der Abstand zwischen den Wirbeln, der dem Abstande zwischen zwei maximalen oder minimalen Werten des Druckes gleich ist, $T$ — die Pulsationsperiode, $t$ — die fliessende Zeit, $x$ — der Abstand des Koordinatenanfanges (stromabwärts) von dem betrachteten Punkte, $P$ — der pulsierende Druck im Punkte $M(x)$ für den Zeitpunkt $t$ sind.

Das Kippmoment der Pulsationskräfte, die an der oberen Oberfläche der $l$-langen Platte, deren vordere Kante die Abscisse $x_1$ hat, angreifen, wird in folgender Weise ausgedrückt (das Moment wird auf die hintere Plattenkante bezogen):

$$M = \int_{x=x_1}^{x=x_1+l} P\,(x_1 + l - x)\,dx. \tag{10}$$

Durch Substitution von (9) und darauffolgende Integration erhält man:

$$M = P_0 \left(\frac{\lambda}{2\pi}\right)^2 \left\{ \sin 2\pi \left(\frac{x_1}{\lambda} - \frac{t}{T}\right) \left[ -2\pi \frac{l}{\lambda} + \sin \frac{2\pi l}{\lambda} \right] + \right.$$
$$\left. + \cos 2\pi \left(\frac{x_1}{\lambda} - \frac{t}{T}\right) \left[ 1 - \cos \frac{2\pi l}{\lambda} \right] \right\}. \tag{11}$$

Durch Differenzierung nach $t$ bestimmen wir auf gewöhnlichem Wege, den nach der absoluten Grösse, maximalen Wert $M_0$ des Moments. Nach Vollziehung der Berechnungen erhält man

$$M_0 = \nu \frac{P_0 l^2}{2} \tag{12}$$

vorin

$$\nu = \frac{\sin\frac{\pi l}{\lambda}}{\left(\frac{\pi l}{\lambda}\right)} \sqrt{\left[\frac{\sin\frac{\pi l}{\lambda}}{\frac{\pi l}{\lambda}}\right]^2 + \frac{1}{\sin^2\left(\frac{\pi l}{\lambda}\right)}\left[1 - \frac{\sin\frac{2\pi l}{\lambda}}{\frac{2\pi l}{\lambda}}\right]^2} \tag{13}$$

Das festhaltende Moment wird durch den Ausdruck

$$M_y = (\gamma_1 - \gamma)\frac{l^2\delta}{2} \tag{14}$$

bestimmt, worin $\gamma$ und $\gamma_1$ — die spez. Gewichte des Wassers und des Plattenbaustoffes, $l$ und $\delta$ — die Länge und die Stärke der Platte bedeuten.

Das Herauskehren der Platte aus ihrem Lager findet dann statt, wenn $M_0 \geqslant M_y$, was auf Grund der Ausdrücke (12) und (14) in folgender Weise hingeschrieben werden kann:

$$P_0 \geqslant (\gamma_1 - \gamma)\frac{\delta}{\nu}. \tag{15}$$

Für die Prüfung der vorgeschlagenen Theorie wurden die Ergebnisse der Versuche bezüglich der Plattenstabilität ausgenützt, die im Wasserbaulaboratorium von «Moskwawolgostroi» im Jahre 1935 vorgenommen wurden. Die Versuchsdata stimmen in genügender Weise mit den theoretischen Folgerungen überein.

Wasserbaulaboratorium des
Kuibyschew-Wasserknotens.

Eingegangen
den 13. V. 1940.

ZITIERTE LITERATUR

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[2] Бриджмен, Анализ размерностей.

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*PHYSICS*

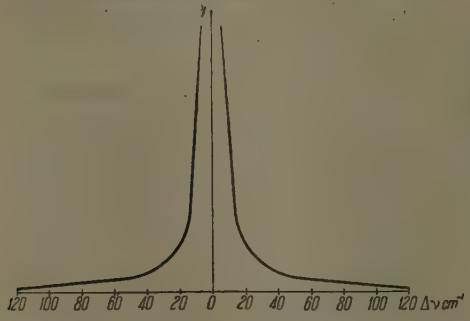
# SCATTERING OF LIGHT AND RELAXATION PHENOMENA IN LIQUIDS

By E. GROSS

*(Communicated by D. S. Rozhdestvensky, Member of the Academy, 4. V. 1940)*

When light is scattered in liquids, radiation is emitted giving rise to a continuous spectrum near the Rayleigh line. This spectrum extends almost symmetrically from the Rayleigh line into both the red and the violet region of the spectrum over a distance of the order of 100 $cm^{-1}$. Thus, an appreciable change in the wave-length of the exciting light is observed in this case. This phenomenon which, to a greater or lesser degree, is common to all liquids, is known as the Rayleigh line «wings».

A number of investigations have established [1] that, as this may be ascertained with the help of a prism spectrograph, the intensity distribution of the continuum near the Rayleigh line is as shown below (Fig. 1)*.




In the immediate vicinity of the Rayleigh line (which is a triplet due to Debye's heat waves and is unresolvable by a prism spectrograph), the intensity of the continuous spectrum is high, and it falls rapidly as the distance from the Rayleigh line increases. The width of this part of the continuous spectrum is insignificant and does not generally exceed a few $cm^{-1}$ (on either side of the Rayleigh line). For liquid benzene, for instance, this region of the continuous spectrum, as measured by Weiler, Bhagavantam and Rao, extends to either side of the Rayleigh line over a distance of about 10—20 $cm^{-1}$. This narrow region of the continuous spectrum of scattering will hereinafter be termed «the Rayleigh line background» (or simply «background»).

As the distance from the exciting frequency increases, the Rayleigh line background is seen on the spectrogram to merge into that portion of the continuous spectrum whose intensity diminishes gradually and which extends

* For example, Fig. 1 shows the intensity distribution for benzene, after the data of Weiler, Bhagavantam and Rao [1].

over a distance of about 100 $cm^{-1}$ from the Rayleigh line. In this article, the term «Rayleigh line wings» (or simply «wings») will be applied only to this second, wider, outer region of the spectrum of scattering of a liquid, to distinguish it from the Rayleigh line background.

Raman and Krishnan [2] interpreted the Rayleigh line wings as the rotation spectrum of scattering, due to rotation of molecules in the liquid. That interpretation was generally adopted. As far back as 1930, however, I suggested [3] a different interpretation for the Rayleigh line wings, assuming them to be of a vibrational, not of a rotational origin. According to that interpretation, the wings are due to thermal vibrations of molecules in the liquid, their extent on the spectrogram being associated by the writer with the maximum frequency of Debye's acoustic spectrum.

The investigations of the influence of temperature on the wings, as well as of the scattering spectra of crystals of organic substances as performed by my co-workers and myself [4], have actually shown that in the main the wings are not produced by molecular rotation in a liquid as it takes place in a gas, but are associated with the low-frequency spectrum of scattering of crystals due to vibrations of the crystal lattice. It is therefore natural to regard the phenomenon of wings as a consequence of the existence of a quasi-crystalline structure in liquids. It is possible to interpret them as a spectrum due to vibrations in the crystal-like structural elements of the liquid, which remain in it after the melting of the crystal.

The present communication deals with that region of the continuous spectrum of scattering of liquids which I have termed the Rayleigh line background.

The nature of this phenomenon has not yet been ascertained. Observations show that the causes giving rise to the Rayleigh line background are different from those responsible for the wings. The experiments of Vuks and myself [5] prove that, corresponding to the Rayleigh line wings in a liquid, there is always to be found, in the same spectral region, a spectrum due to the crystal lattice (low-frequency spectrum). No phenomenon, however, corresponding to the Rayleigh line background has so far been detected with certitude in the crystal. That phenomenon would appear to be characteristic of the liquid state. Moreover, the experiments of Vuks and myself have shown [6] that, while a rise in the temperature of the liquid does not appreciably affect the wings, it causes the background to increase in intensity and to extend farther away from the exciting frequency.

The Rayleigh line background is undoubtedly a direct extension of the continuous spectrum which I had been able to detect [7] with the help of spectral apparatus of high resolving power and which underlies the Rayleigh line components due to Debye's heat waves. The intensity of both phenomena is closely connected with the optical anisotropy of the molecules of the liquid. Both spectra generally exhibit a high intensity for liquids having a great optical anisotropy. Being essentially one and the same phenomenon, they undoubtedly are of the same origin.

What then is the nature of that phenomenon?

Some writers [8] endeavour to attribute also this portion of the continuous spectrum near the Rayleigh line to the free rotation of molecules in the liquid. To my mind, this view is untenable. Neither from the point of view of the distribution of intensity nor from that of its magnitude can the Rayleigh line background be identified with the rotational Raman spectrum. The mechanism of its occurrence calls, in my opinion, for a different explanation, an outline of which is given below.

The «coherent» scattering of light in pure liquids is known to be due in the main to two factors: the fluctuations of density, and the fluctuations

in orientations of the anisotropic molecules in the liquid. The intensity of the scattered light due to orientation fluctuations depends on the optical anisotropy of the molecules of the liquid. For highly anisotropic molecules, this kind of scattering may amount to a very large portion of the integral intensity of the scattered light. The orientation fluctuations are not constant, but vary in time owing to thermal motion. Changes in the orientations of the molecules occurring during the process of the scattering of light should produce changes in the frequency of scattered light*, and these to my mind are responsible for the Rayleigh line background on the scattered light spectrogram.

The presence in liquids of a Rayleigh line structure due to heat waves shows that Debye's conception of a random thermal motion in solids as a superposition of elastic vibrations is largely justified for the liquid state as well. The molecules of a liquid are, as a rule, elongated or flattened-out formations. It is therefore natural to suppose that, simultaneously with shifting of the centres of gravity, the turning of such molecules will take place. The contraction of an elastic wave will cause the molecule to turn in one direction, the expansion of the wave will turn it in the opposite direction. Thus, a Debye heat wave of a certain frequency propagating in the liquid will not only subject the molecules to translational motion, but the latter will, simultaneously with that motion, also perform angular oscillations of the same frequency. These angular oscillations of varying frequencies will be performed by the molecules in time with the vibrations of all the elastic heat waves of the acoustic spectrum of the liquid. There is therefore present in a liquid a whole spectrum of angular oscillations of every possible frequency, a spectrum identical with Debye's acoustic spectrum.

The molecules being optically anisotropic, the amplitude of the light scattered by a particular molecule will depend on the orientation of its axes with respect to the vector of the exciting light. The rotational oscillations of the anisotropic molecules periodically change the amplitude of the scattered light and will therefore produce changes in the frequency of the exciting light.

The fluctuations in the orientation of molecular axes in a liquid are distributed at random and are independent of one another. The components of the depolarized light scattered by oscillating anisotropic molecules will be uncorrelated** for the different orientation fluctuations. Frequency changes of the incident light will therefore be produced by the whole spectrum of the angular oscillations of the molecules, according to the ratio:

$$\nu = \nu_0 \pm \omega_i$$

where $\nu_0$ is the frequency of the exciting light, $\nu$—the frequency of the scattered light, $\omega_i$—the frequency of the angular oscillations of the molecule.

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* In the same way as changes in density fluctuations in time, due to thermal motion, give rise to the occurrence of structure in the Rayleigh line.

** As are the components of the polarized light scattered by density fluctuations due to the superposition of Debye's heat waves. Light waves scattered by periodically distributed density fluctuations, forming a separate train of heat waves of definite frequency and direction, are correlated in phase and are therefore capable of interfering with each other. Therefore, it is only those heat waves whose wave-length is in a definite relation to the wave-length of light (Bragg's condition for the space lattice) that give rise to any appreciable scattering of light. This accounts for the discrete components of the Rayleigh line appearing in the spectrum of scattered light.

This limitation is non-existent in the case of scattering due to fluctuations in the orientation of the molecules. Owing to the angular oscillations of the molecules, the whole complex of heat waves of Debye's acoustic spectrum may be revealed in the spectrum of scattered light (in this case, as shown below, the limitation is determined by the relaxation phenomena in the liquid).

A spectrogram of scattered light should therefore show a depolarized continuous spectrum, beginning from the undisplaced line and extending on either side of the Rayleigh line towards the long and the short waves. This is the continuous spectrum that I have termed the Rayleigh line background. The extent of this spectrum, beginning from the Rayleigh line, should be determined by the relaxation phenomena in the liquid.

When rotational oscillations of molecules due to thermal waves take place, a certain distribution of the axes of the molecules in the liquid will be established at every moment. The re-arrangement of the axes of the molecules requires a certain time depending on the friction in the liquid. The establishment of a certain orientation of the molecules in a liquid in their angular oscillations due to heat waves may thus be characterized by a certain relaxation time $\tau$.

For this reason, not all the frequencies are necessarily present in the spectrum of angular oscillations of the molecules of a liquid.

In the propagation of such heat waves of period $T$, for which $T \gg \tau$, the molecules of the liquid will be able to re-arrange themselves during the time elapsing between the consecutive phases of an elastic wave. Angular oscillations of period $T \gg \tau$ will therefore take place in the liquid. The axes of the molecules will therefore have the time to rotate through a rather large angle. The amplitude of the light scattered by the molecules of the liquid performing such angular oscillations will change periodically, changes in the frequency of the incident light being observed.

When heat waves of period $T \ll \tau$ are propagated, the axes of the molecules do not have the time to rotate through an appreciable angle and perform angular oscillations in time with vibrations of the elastic waves. The spectrum of the angular oscillations of the molecules in the liquid will contain no oscillations of period $T \ll \tau$ of appreciable intensity. No changes in the amplitude of the light scattered by the molecules will take place in this case, so that no scattered light of altered frequency will be observed.

An intermediate case will take place for oscillations of period $T \approx \tau$. In the spectrum angular oscillations of the molecules, oscillations of frequencies lying within this range already begin to grow small as frequency is increased. Therefore, in the case of such frequencies of the angular oscillations of the molecules, the amplitude of the scattered light changes but little.

Hence it follows that the intensity of the Rayleigh line background should strongly decrease and become very low at such distances from the Rayleigh line as correspond to the frequencies of angular oscillations of the order of $\frac{1}{\tau}$ and greater.

It may be seen from the above that the processes bound up with the turning of molecular axes due to propagation of heat waves are analogous to phenomena taking place in polar liquids and due to the turning of polar molecules under the orientating action of a high frequency electric field. The time of relaxation $\tau$ involved in these processes is therefore the time of relaxation introduced by Debye in working out the theory of the dielectric properties of liquids in high frequency fields, i. e.

$$\tau = \frac{8\pi\eta a^3}{2kT} \qquad (1)$$

where $\eta$ is the viscosity of the liquid, $a$—the radius of the molecule, $T$—absolute temperature, $k$—Boltzmann's constant.

The intensity of the background thus depends on the optical anisotropy of the molecules, its extent in the scattered light spectrogram being also

determined by viscosity, temperature, and the size of the molecules of the liquid.

The above interpretation of the Rayleigh line background is confirmed by experimental data. All the characters of this background so far ascertained become comprehensible if considered from this point of view. A high intensity of the phenomenon in liquids whose molecules have a high degree of optical anisotropy is directly deducible from the above considerations. No Rayleigh line background is observed in crystals, owing to the absence of such fluctuations in molecular orientation in the lattice as would be independent from one another. .

The new point of view on the origin of the Rayleigh line background is confirmed by experiments on the influence of temperature on the background, while these experiments themselves find an explanation from that point of view. As shown by my own experiments with xylene, subsequently confirmed by those made with diphenyl ether and benzophenone by Vuks and myself (⁸), the heating of these liquids gives rise to an appreciable broadening of the Rayleigh line background (an increased intensity at the «edges» of the background). This extension of the background to a greater distance from the Rayleigh line is due to the fact that the time of relaxation of the molecules of a liquid grows shorter as temperature is increased. As this may be seen from formula (1), the dependence of $\tau$ on time is a double one, viz., a direct one, and through viscosity $\eta$. If, therefore, temperature rises and the viscosity of the liquid decreases, the «edges» of the background are shifted farther away from the Rayleigh line, as the angular oscillations of the molecules of the higher frequencies become more intensive in the liquid.

An increase in the viscosity of the liquid should cause the Rayleigh line background to shrink and its «edges» to approach the Rayleigh line. For those liquids, for which $\tau$ is large enough, no background should be observable with the help of a prism spectrograph of medium dispersion. I have in fact failed to observe, with a prism spectrograph, any appreciable Rayleigh line background in such a liquid as benzyl alcohol whose viscosity is fairly high.

In mixtures of liquids and in solutions, the extent of the background is also determined by their viscosity. The solutions of substances having anisotropic molecules in non-viscous solvents should have an appreciable Rayleigh line background. No background, however, should be observable in solutions of such substances in sufficiently viscous solvents.

The «edges» of the Rayleigh line background, where its intensity in the spectrogram grows low, correspond, as stated above, to frequencies $\nu$ of the spectrum of angular oscillations, determined by the ratio:

$$\nu \approx \frac{2kT}{8\pi\eta a^3} = \frac{1}{\tau}.$$

By determining the position of the «edge» of the background in the spectrogram* we can thus estimate the time of relaxation of molecules of the liquid.

The table shows the time of relaxation for the molecules of some liquids, as determined by the writer from observations of the Rayleigh line back-

* This determination could, of course, be made only approximately, the «edges» of the background in the spectrogram being blurred. Besides, the wings are usually partly superimposed on the background. In the measurements made, the edge of the background was taken to be that region of the spectrogram, where the intensity of the background did not differ from that of the wings, the background being merged with the wings. A more accurate determination of $\tau$ from observations of the Rayleigh line background can only be made upon analyzing the decrease of the intensity towards the edges of the background. Such an analysis will be made in our subsequent investigations.

ground. In the same table are shown, for comparison, the values of the time of relaxation determined from observations of the dielectrical properties of liquids in accordance with Debye's theory ([10]).

| Substance | Scattering of light $\tau \times 10^{11}$ | Debye's theory $\tau \times 10^{11}$ |
|---|---|---|
| Chlorbenzene . . . . | 0.2 | 0.64 |
| *o*-dichlorbenzene . . | 0.3 | 1.03 |
| Benzene . . . . . | 0.15 | — |

It may be seen from the table that an estimation of the time of relaxation based on observations of the Rayleigh line background yields values of the same order as those of Debye's theory.

It may be seen from the above that the explanation suggested in this paper for the origin of the Rayleigh line background is confirmed experimentally. The investigation of the Rayleigh line background supplies a new spectroscopic method for the determination of the time of relaxation for the molecules of a liquid. This method is also applicable to non-polar liquids.

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*PHYSIQUE*

# SUR LA VITESSE DE PROPAGATION DU SON DANS LE QUARTZ

Par K. WULFSON

*(Présenté par S. I. Wawilow, de l'Académie, le 16. V. 1940)*

L'étude expérimentale de la structure fine du spectre de dispersion de Rayleigh dans les cristaux fait croire que le spectre de la lumière dispersée a plusieurs paires de composantes déplacées, au lieu d'une seule paire comme on le croyait auparavant ([1],[2]).

Gross ([3]) indique dans son article qu'on peut distinguer sur les photographies trois paires de composantes déplacées, qu'il attribue aux trois types d'oscillations acoustiques ayant lieu dans un cristal anisotrope. En partant de la valeur de la désaggrégation et en utilisant la relation connue

$$\Delta\nu = \pm 2\nu_0 n \frac{v}{c} \sin\frac{\theta}{2} \qquad (1)$$

Gross détermine la vitesse de propagation de ces oscillations:

$v_1 = 6400$m/sec., $v_2 = 3500$ m/sec., $v_3 = 2800$ ou $4600$ m/sec*.

Dans les nombreuses sources littéraires consacrées aux oscillations du quartz il y a très peu de données sur la vitesse de propagation des ondes sonores dans le quartz. Quelques rares données ([4]) qu'on trouve se distinguent beaucoup les unes des autres. Ceci paraît d'autant plus étonnant que les constantes élastiques et la densité du quartz (déterminant la vitesse du son) ont été établies avec une précision suffisante et on n'a pas de raison de supposer qu'elles puissent varier d'un échantillon à l'autre.

On sait de la théorie de propagation des oscillations élastiques dans le milieu anisotrope ([5]) que dans chaque direction peuvent se propager trois ondes, dont les vitesses sont définies par les racines de l'équation séculaire:

$$\begin{vmatrix} \lambda_{11}-c^2\rho & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \lambda_{22}-c^2\rho & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \lambda_{33}-c^2\rho \end{vmatrix} = 0 \qquad (2)$$

où $\rho$ est la densité, $c$—la vitesse du son.

$$\lambda_{11} = C_{11}l^2 + C_{66}m^2 + C_{55}n^2 + 2C_{56}mn + 2C_{13}nl + 2C_{16}lm$$
$$\lambda_{22} = C_{66}l^2 + C_{22}m^2 + C_{44}n^2 + 2C_{24}mn + 2C_{46}nl + 2C_{26}lm$$
$$\lambda_{33} = C_{55}l^2 + C_{44}m^2 + C_{33}n^2 + 2C_{34}mn + 2C_{35}nl + 2C_{45}lm$$
$$\lambda_{12} = C_{16}l^2 + C_{26}m^2 + C_{45}n^2 + (C_{46}+C_{35})mn + (C_{14}+C_{56})nl + (C_{12}+C_{66})lm$$
$$\lambda_{13} = C_{15}l^2 + C_{46}m^2 + C_{35}n^2 + (C_{36}+C_{45})mn + (C_{13}+C_{55})nl + (C_{14}+C_{56})lm$$
$$\lambda_{23} = C_{56}l^2 + C_{24}m^2 + C_{34}n^2 + (C_{44}+C_{23})mn + (C_{36}+C_{45})nl + (C_{46}+C_{35})lm.$$

Dans ces formules $C_{ik}$ désigne les constantes élastiques, $l$, $m$, $n$—les cosinus des angles entre les axes des cristaux et la direction de propagation des ondes acoustiques. Nous avons effectué les calculs relatifs aux

* Les valeurs données s'obtiennent de l'interprétation la plus probable des interférences observées. Malheureusement, cette interprétation n'est pas unique, car l'on trouve pour $v_3$ deux valeurs. Cette détermination double rend la vérification de la théorie extrêmement difficile.

directions les plus caractéristiques pour la propagation du son. Les résultats obtenus sont donnés dans le tableau.

| Constantes élastiques en $\frac{\text{dyne}}{\text{cm}^2}$ | Direction de propagation | Vitesse du son en m/sec. | | |
|---|---|---|---|---|
| $C_{11}=C_{22}=852\cdot10^9$<br>$C_{33}=1084.5\cdot10^9$<br>$C_{44}=C_{55}=571.5\cdot10^9$ | Le long de l'axe électrique $X$<br>$l=1,\ m=n=0$ | 4200 | 3850 | 3060 |
| $C_{66}=\frac{1}{2}(C_{11}-C_{12})=391.2\cdot10^9$<br>$C_{12}=69.5\cdot10^9$<br>$C_{13}=C_{23}=141\cdot10^9$<br>$C_{15}=C_{25}=C_{46}=-168.3\cdot10^9$<br>$C_{14}=C_{16}=C_{56}=0$<br>$p=2.65$ | Le long de l'axe mécanique $Y$<br>$l=n=0,\ m=1$ | 5680 | 3565 | 2340 |
| | Le long de l'axe optique $Z$<br>$l=m=0,\ n=1$ | 6460 | 4650 | 4650 |

On voit du tableau que la vitesse de propagation dépend beaucoup de la direction. Il est possible que cela explique la divergence des données obtenues par de différents expérimentateurs. La même raison cause la nécessité d'effectuer les études de la structure fine du spectre de la lumière dispersée avec des échantillons ayant une orientation déterminée de ses trois axes cristallographiques. Il faut s'attendre, par exemple, dans un morceau de quartz, coupé de façon que l'axe optique forme un angle de 45° avec la direction du rayon primitif et dispersé, qu'il n'y aura que deux couples de composantes correspondant à deux vitesses 6460 et 4650 m/sec. Il en résultera une simplification du tableau de l'interférence.

Si l'on compare les valeurs des vitesses trouvées par Gross avec celles données dans le tableau, on voit, en admettant $v_3$ égale à la seconde valeur possible—4600 m/sec., que les vitesses des deux ondes coïncident à 1—2% près avec la vitesse calculée pour le cas de propagation le long de l'axe optique. Quant à la troisième vitesse de propagation, trouvée par Gross, elle coïncide avec celle calculée pour le cas de propagation le long de l'axe mécanique. Une bonne coïncidence des vitesses $v_1$ et $v_3$ avec les valeurs calculées indique peut-être que l'orientation de l'échantillon était telle que les ondes élastiques, qui causent la dispersion de la lumière, se propageaient dans la direction formant un petit angle avec l'axe optique.

Malheureusement, Gross ne dit rien dans son article ([3]) sur la direction de propagation des ondes élastiques. Mais on peut tout de même s'attendre qu'en résolvant l'équation (2) pour les valeurs des cosinus directeurs $l$, $m$, $n$ correspondant à l'échantillon utilisé, on pourra arriver à la coïncidence du calcul avec les données expérimentales pour les trois vitesses en même temps.

Les valeurs trouvées par nous au moyen de l'équation (2) coïncident mieux avec les valeurs expérimentales, que celles calculées par Gross d'après les formules approximatives ($v_1=6800$; $v_2=3700$; $v_3=3300$).

Par conséquent, la solution de l'équation (2) donne une confirmation plus sûre de l'hypothèse faite par Gross, que la structure plus complexe des raies de Rayleigh est due à la présence de trois oscillations acoustiques différentes dans un cristal anisotrope.

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*CHEMISTRY*

# KINETICS OF DEHYDROGENATION OF SECONDARY BUTYL ALCOHOL AND REVERSIBLE POISONING OF COPPER CATALYSTS

By A. A. BALANDIN and A. L. LIBERMAN

*(Communicated by N. D. Zelinsky, Member of the Academy, 5. VII. 1940)*

The effect of reversible poisoning of copper catalysts on the kinetics of dehydrogenation of primary and secondary alcohols was studied by a number of investigators both from theoretical and from practical point of view (1, 2). Equations derived by those authors show that for exact understanding of the mechanism of reversible poisoning, as well as for a measurement of the heats of activation of any heterogeneous reactions, a knowledge of relative mean lives of molecules of the reactants, the reaction products and admixtures on active centres of the catalyst is necessary.

At the Laboratory of Organic Catalysis, Moscow State University, a method of measuring relative mean lives of molecules on active centres and of true heats of activation was developed. The runs are carried out by the flow method and the calculations are based on the equation (3)

$$\frac{dm}{dt} = k_1 \frac{\alpha_1 (M - m)}{1 + \alpha_1 (M - m) + \alpha_2 m + \alpha_3 m} \qquad (1)$$

where $M$ is the number of mls of the vapour of the reactant introduced into the catalyst tube per unit time, $m$ is the number of mls of the vapour of reaction products leaving the tube per unit time, $\alpha_1$, $\alpha_2$, $\alpha_3$ are the adsorption coefficients of the reactant and reaction products, respectively, and $k_1$ is the constant proportional to the constant of reaction velocity.

After certain transformations and integration of equation (1) the following expression was obtained:

$$k = m \left[ M + \left( \frac{\alpha_2}{\alpha_1} + \frac{\alpha_3}{\alpha_1} - 1 \right) \frac{m}{2} \right] \Big/ \left( M - \frac{m}{2} \right). \qquad (2)$$

As it was shown (2), in case of dehydrogenation of primary alcohols

$$\alpha_2 \approx \alpha_1 \quad \text{and} \quad \alpha_3 \approx 0 \qquad (3)$$

where $\alpha_1$, $\alpha_2$, and $\alpha_3$ refer to alcohol, aldehyde and hydrogen, respectively. Then (2) is transformed into

$$k = mM \Big/ \left( M - \frac{m}{2} \right) \qquad (4)$$

where the adsorption coefficients are no longer included.

This equation afforded the possibility ([3]) of measuring true heats of activation of dehydrogenation of ethyl alcohol, which were found to amount to 12800 cal. per mole, and analogously those of the next members of the homologous series.

In the light of these data it was of interest to measure on the surface of copper the relative mean lives of molecules of secondary alcohols and their dehydrogenation products, i. e. the corresponding ketones, and to find the true heat of activation of this reaction, too.

In literature only contradictory data are met with: that the ketone is adsorbed more strongly ([4]), or, on the contrary, somewhat less strongly (with almost identical strength) ([5]).

The data on the heat of activation of dehydrogenation of secondary alcohols are also contradictory, which was explained ([5]) by non-uniformity of the methods of preparing the catalysts. As it became recently known ([6]), the heat of activation depends on the degree of dispersion of the catalyst; it may be supposed therefore that according to the conditions of reduction catalysts of various dispersion had been obtained. Palmer and Constable ([4]) found for copper reduced with carbon monoxide at 300°, the value 22000 cal. per mole; one of us, Marushkin and Ikonnikov ([5]) found 14000 cal. per mole for apparent heat of activation of isopropyl alcohol and of cyclohexanol on copper reduced by hydrogen at 350°. Bork used these data to compute the true heat of activation which was found to be 16355 cal. per mole. For cyclohexanol on copper reduced with hydrogen the temperature having been gradually increased from 300 to 350°, the value 7270 cal. per mole was found ([7]).

All these values differ from the heats of activation of primary alcohols and are little comparable with them. In order to be able to make this comparison, the authors have operated under identical conditions of experiments carried out at the same time and almost side-by-side with the experiments with primary alcohols ([3]). Identical apparatus, the same initial products used for preparation of the catalysts, the same method of their preparation and conducting the experiments ensured a comparability of the results obtained with primary and secondary alcohols.

Contrary to the facts observed in a study on ethyl alcohol, a considerable irreversible poisoning was observed in the case of dehydrogenation of secondary butyl alcohol on copper (particularly above 240°). Naturally enough, it led to considerable inconvenience. We have succeeded in securing from 75 runs only 3 adequately complete series of runs; the results are described below. The same reason prevented us from experimental determination of $\alpha_2/\alpha_1$ and $\alpha_3/\alpha_1$ in this case.

Recently Bork ([8]) succeeded in discovering by indirect method that for the secondary butyl alcohol, too, $\alpha_2/\alpha_1=1$ and $\alpha_3/\alpha_1=0$. Hence the equation (4) must remain valid in this case. At any rate, the absence of adsorption factors in the velocity constant which follows from this fact affords a possibility of computing true heats of activation of dehydrogenation of secondary butyl alcohol on copper catalyst.

The dependence of reaction velocity on the rate of passage of the reactant has been investigated but scarcely, if at all. Theoretically it should obey the equation (4). In this case by plotting $\frac{1}{m}$ against $\frac{1}{M}$ a straight line should be obtained, inasmuch as from equation (4) we obtain

$$\frac{1}{m}=\frac{a}{M}+\frac{1}{k} \qquad (5)$$

where $a=0.5$ according to equation (4). By putting $k$ from (5) into Arrhenius' equation, the true heat of activation may be found.

A p p a r a t u s. The runs were carried out by the flow-method in an apparatus described earlier ([9]) with the following modifications: 1) the temperature was measured by a thermocouple (copper-constantan) in the middle of the catalyst layer, a special sheath for the thermocouple having been sealed into the catalyst tube. 2) The main part of the apparatus for measuring the volume of evolving gas was a 300 ml burette with marks after every 0.5 ml; this apparatus was mounted completely with groundjoint connexions. 3) The apparatus for measuring the gas volume was provided with a valve for preventing back-sucking of the gas into the catalyst space. The inner diameter of the catalyst tube was 1.8 cm. The deviations of the temperature along the length of the furnace did not exceed $\pm 1°$ over a length of 60 cm.

S e c o n d a r y B u t y l A l c o h o l. The alcohol, obtained from the Institute of Pure Chemical Reagents, was subjected to additional purification. With that aim it was thrice fractionated with a column, described by Galpern ([10]), having the working section of 1.5 m. The product obtained after third fractionation passed totally (1700 ml) at 99.8 to 99.9° (at 760 mm) and had $d_4^{20}=0.8067$ and $n_D^{20}=1.3971$. $MR_D$ found=22.12, calculated for $C_4H_9OH=22.20$.

In order to ascertain whether it was not the possible insignificant admixture of unsaturated alcohols to the secondary butyl alcohol that caused the irreversible poisoning, part of the latter alcohol was passed in an atmosphere of $H_2$ at 150° over Ni deposited on asbestos. However, even after this treatment the alcohol continued to cause irreversible poisoning of the catalyst with the same ease as before.

P r e p a r a t i o n o f t h e C a t a l y s t. The catalyst was prepared by heating copper nitrate in a copper crucible till nitrogen oxides ceased to escape. Then the resulting copper oxide was crushed in an agate mortar into fine powder, and separate portions of this latter were reduced in a stream of $H_2$ at 250° in the catalyst tube itself. The catalyst was of brick-red colour and subjected to spontaneous warming in the air. In all experiments the length of the layer of the catalyst was 1 cm.

D e p e n d e n c e o f R e a c t i o n V e l o c i t y o n t h e R a t e o f P a s s a g e. During every run the alcohol was added from the burette at a constant rate; hydrogen was also found to evolve at a constant rate. An example is given in Table 1. By altering the rate of passage of the alcohol from run to run we have obtained the data of the Table 2.

Table 1

D e g r e e o f C o n s t a n c y o f G a s E v o l u t i o n D u r i n g E x p e r i m e n t
(Run No. 22; temperature of the run—242°; mean rate of evolution of hydrogen 17.36 ml per 3 min.)

| Time, min. | Volume of alcohol added, ml | Volume of hydrogen evolved, ml | Diff. | Time, min. | Volume of alcohol added, ml | Volume of hydrogen evolved, ml | Diff. |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 18 | 3.3 | 105.8 | 15.5 |
| 3 | 0.5 | 18.5 | 18.5 | 21 | 3.9 | 124.8 | 19.0 |
| 6 | 1.1 | 36.8 | 18.3 | 24 | 4.4 | 140.8 | 16.0 |
| 9 | 1.6 | 54.8 | 18.0 | 27 | 5.0 | 156.0 | 15.2 |
| 12 | 2.2 | 72.5 | 17.7 | 30 | 5.5 | 173.6 | 17.6 |
| 15 | 2.8 | 90.3 | 17.8 | | | | |
| | | | | | | Mean.. | 17.35 |

A straight line actually resulted when the equation (5) was applied to these data (Fig. 2). However, the coefficient $a$ instead of the expected 0.5 was almost exactly equal to 2 ($a=2.03$; $k=17.39$). In other words, the resulting data satisfied the equation

$$k' = \frac{mM}{M-2m}. \qquad (6)$$

This result is of considerable interest for our knowledge of the kinetics of reactions by the flow method.

Table 2

Volume of Evolving Hydrogen Depending on the Rate of Passage of the Alcohol ($T = 241.5$—$243.0°$ C; data for the intervals of 3 min.; $k' = 17.39$, $a = 2.03$)

| Run No. | Rate of passage of the alcohol, ml | Volume of hydrogen evolved, ml | $k'$ according to eq. (6) | Run No. | Rate of passage of the alcohol, ml | Volume of hydrogen evolved, ml | $k'$ according to eq. (6) |
|---|---|---|---|---|---|---|---|
| 39 | 0.17 | 9.9 | 19.50 | 37 | 0.61 | 12.9 | 15.60 |
| 32 | 0.33 | 12.1 | 17.24 | 33 | 1.06 | 15.3 | 17.35 |
| 30 | 0.48 | 13.5 | 17.51 | 34 | 1.38 | 15.9 | 17.61 |
| 31 | 0.49 | 13.6 | 17.75 | 38 | 1.77 | 16.3 | 17.65 |
| | | | | | | Mean | 17.60 |

The problem of dependence of reaction velocity on the rate of passage deserves further investigation.

Dependence of the Reaction Velocity on Temperature. Under the conditions described earlier we have obtained results of 2 series of runs with 2 preparations of copper catalyst reduced by hydrogen at 250°. The length of the catalyst layer was 1 cm. The experiment had been undertaken in order to ascertain the dependence of reaction

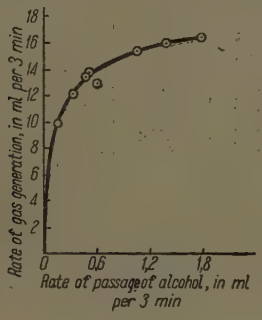

Fig. 1.

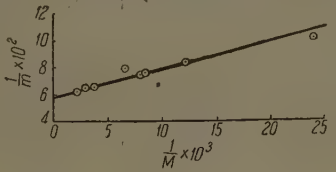

Fig. 2.

velocity on temperature. The results are given in Tables 3 and 4. The values $M$ and $m$ (for 3 min. intervals) obtained at different temperatures are shown therein. The reaction velocity constants have been computed from the experimental data both from equation (4), $k$, and from equation (6), $k'$. These values are also given in Tables 3 and 4. The true heat of activation $Q = 9050$ cal. per mole and pre-exponential member $k_0 = 1.08 \times 10^5$ for runs Nos. 13 to 18, and $Q = 8370$ and $k_0 = 6.43 \times 10^4$ for runs Nos. 22 to 26, have been computed from $k$. Analogously $Q = 10450$ and $k_0' = 5.07 \times 10^5$ for runs Nos. 13 to 18, and $Q = 10150$ and $k_0' = 4.50 \times 10^5$ for runs Nos. 22 to 26 have been computed from $k'$. Values $k$ and $k'$ have been recomputed from the latter data (Tables 3 and 4). As seen from the tables, values $k$ and $k'$ obtained in this way are in good agreement with the observed ones.

Notice should be taken of the fact that the heat of activation computed from equation (4) and that from equation (6) do not differ greatly. Furthermore, $k$ and $k'$ are in both cases in good agreement with Arrhenius' equation; it is seen from Figs. 3 and 4 (straight lines). On the other hand, straight lines were not obtained when log $m$ was plotted against $\frac{1}{T}$ in the same Figs. 3 and 4, demonstrating the advantage of using equations (4) and (6). It is of some interest that $k'_0$ computed from equation (6) in Tables 3 and 4 do not

Table 3

$Q$=9050 cal. per mole and $k_0=1.08\times10^5$ from eq. (4) and $Q$=10450 cal. per mole and $k'_0=5\cdot07\times10^5$ from eq. (6) (all gas volumes are in NTP)

| Run No. | Temperature, °C | Rate of passage of alcohol, ml | $M$, ml | Volume of $H_2$, $m$ in ml | $k$ obs. from eq. (4) | $k$ calc. for $Q$=9 050 | $k'$ obs. from eq. (6) | $k'$ calc. for $Q$=10 450 |
|---|---|---|---|---|---|---|---|---|
| 18 | 203.1 ± 0.4 | 0.69 | 168.36 | 7.18 | 7.34 | 7.48 | 7.85 | 8.00 |
| 17 | 221.3 ± 0.4 | 0.60 | 146.40 | 10.46 | 10.84 | 10.67 | 12.20 | 12.02 |
| 16 | 239.5 ± 0.1 | 0.66 | 161.04 | 13.90 | 14.53 | 14.79 | 16.80 | 17.54 |
| 15 | 241.5 ± 0.4 | 0.51 | 124.44 | 14.70 | 15.62 | 15.31 | 19.26 | 18.24 |
| 13 | 242.0 ± 1.0 | 0.51 | 124.44 | 14.10 | 14.95 | 15.45 | 18.23 | 18.45 |

Table 4

$Q$=8370 cal. per mole and $k_0=6.43\times10^4$ from eq. (4) and $Q$=10150 cal. per mole and $k'_0=4.59\times10^5$ from eq. (6) (all gas volumes are in NTP)

| Run No.* | Temperature, °C | Rate of passage of alcohol, ml | $M$, ml | Volume of $H_2$, $m$ in ml | $k$ obs. from eq. (4) | $k$ calc. for $Q$=8 370 | $k'$ obs. from eq. (6) | $k'$ calc. for $Q$=10 150 |
|---|---|---|---|---|---|---|---|---|
| 24 | 204.0 ± 1.0 | 0.69 | 168.36 | 9.11 | 9.36 | 9.31 | 10.22 | 10.16 |
| 23 | 204.2 ± 0.3 | 0.75 | 183.00 | 9.32 | 9.56 | 9.35 | 10.38 | 10.21 |
| 28 | 218.0 ± 0.2 | 0.48 | 117.12 | 10.70 | 11.26 | 12.02 | 13.09 | 13.83 |
| 22 | 241.6 ± 0.1 | 0.54 | 131.76 | 17.36 | 18.58 | 17.78 | 23.57 | 22.23 |
| 25 | 242.0 ± 0.3 | 0.48 | 117.12 | 16.36 | 17.59 | 17.86 | 22.70 | 22.39 |
| 26 | 243.0 ± 0.3 | 0.57 | 139.08 | 19.08 | 18.31 | 18.15 | 22.82 | 22.86 |

much differ from each other, whereas $k'_0$ computed from equation (4) have different order of the value. This testifies to a better applicability of equation (6), inasmuch as in the runs Nos. 13 to 18 and 22 to 26 the quantities of the catalyst and the methods of its preparation were identical and, therefore, the values of the pre-exponential member should be near to each other.

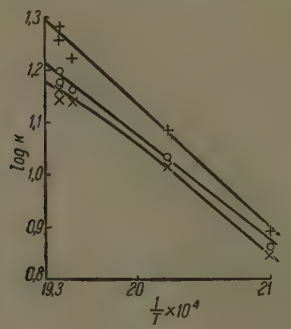


Fig. 3.

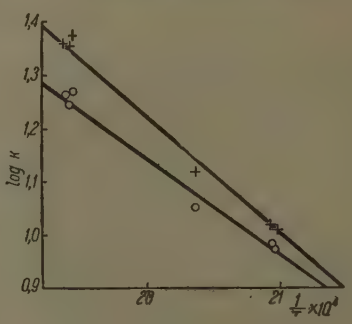


Fig. 4.

We are able to compare the heat of activation of the secondary butyl alcohol, $Q$=8.6 kg cal. per mole, with that of the primary alcohols for which the mean value of $Q$ is 12.8 kg cal. per mole. Both values were obtained with

* Run No. 28 showed too low results on account of some little irreversible poisoning which happened during run No. 27 carried out at a higher temperature (255°).

a catalyst prepared in the same way and computed by means of the same equation (4).

Thus, the heats of activation of secondary alcohols are lower than those of the primary ones. This experimental result is of high importance for the theory of dehydrogenation catalysis.

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*CHEMISTRY*

# APPLICATION OF THE IODATE METHOD TO THE SEPARATION AND DETERMINATION OF RARE ELEMENTS

By T. A. USPENSKAYA and J. A. CHERNIKHOV

*(Communicated by N. S. Kurnakov, Member of the Academy, 9. VII. 1940)*

Iodate is widely used as an oxidizing agent in chemical analysis.

Aside from its oxidizing properties iodate gives sparingly soluble compounds with many elements. Kolthoff (volumetric analysis) mentions that such elements as cupric copper, silver, thallium, lead, barium and strontium can be determined iodometrically after being precipitated as iodates.

Brinton and James determine cerium, and Meyer and Schpetter determine thorium by precipitating these elements with iodate and finishing the determination by reprecipitating the precipitates with oxalic acid. The authors were successful in obtaining precipitates of cerium and thorium iodates of constant composition, corresponding to the following empiric formula:

$$2\,Ce(IO_3)_4KIO_3 \cdot 8\,H_2O \quad \text{and} \quad 4\,Th(IO_3)_4KIO_3 \cdot 18\,H_2O.$$

In view of this they were able to propose a gravimetric and a volumetric method of determining cerium and thorium directly as iodates([1]). The advantage of the volumetric method is its high sensitivity. One part of cerium corresponds to 28 equivalents of iodine, and one part of thorium—to 25.5 equivalents. This makes it possible to apply the iodate method in determining tenths and hundredths of a milligram of cerium and thorium (microquantities).

The authors have worked out a method of determining zirconium analogously to cerium and thorium. As far back as 1889 Davis used sodium iodate to precipitate zirconium. This method abuts on changing the iodate precipitate into zirconium oxide. In this case also the authors were successful in producing a zirconium iodate of constant composition, having the following empiric formula:

$$2\,Zr(IO_3)_4KIO_3 \cdot 8\,H_2O.$$

In the volumetric analysis one part of zirconium corresponds to 27 equivalents of iodine: 1 ml of 0.1 *N* $Na_2S_2O_3$ corresponds to 0.3378 mg zirconium.

The iodate is of great importance in analyzing earthy acids (tantalum and niobium). Applying the method suggested by us in a previous paper for determining cerium and thorium, we were successful in extracting tantalum quantitatively from its oxalate complex* as a compound of constant compo-

* The concentration of oxalate in the test solution should not exceed 2%.

sition. The exact composition of this compound has not as yet been established by the authors. But on the basis of the results obtained from iodometric titration of the precipitates an empiric factor has been deduced for determining tantalum volumetrically (Table 1). Under the conditions of the above experiments 1 ml of 0.1 *N* $Na_2S_2O_3$ corresponds on the average to 1.51 mg of tantalum. Hence it follows that the ratio between tantalum and the iodate ion in the resulting compound equals 1 Ta : 2 $IO'_3$, or 1 part of tantalum in iodometric analysis corresponds to 12 equivalents (181.4/ 15.1 = 12).

Niobium cannot be precipitated with iodate under the conditions applied for precipitating tantalum. Only tantalum is precipitated from solutions containing both elements, and the ratio between tantalum and the iodate ion remains 1 : 2 (Table 2).

Table 1

Establishment of Factor for Volumetric Determination of Tantalum

| Tantalum taken, mg | 0.1 *N* $Na_2S_2O_3$ expended, ml | 1 ml 0.1 *N* $Na_2S_2O_3$ corresponds to mg tantalum |
|---|---|---|
| 4.48 | 2.95 | 1.52 |
| 5.98 | 3.90 | 1.52 |
| 7.92 | 5.20 | 1.53 |
| 8.96 | 5.96 | 1.50 |
| 13.37 | 8.80 | 1.52 |
| 17.71 | 11.80 | 1.50 |
| 25.40 | 16.91 | 1.50 |
| 30.30 | 20.10 | 1.51 |
| | Average | 1.51 |

Table 2

Determination of Tantalum in the Presence of Niobium

| Taken | | 0.1 *N* thiosulphate expended, ml | Tantalum, found*, mg |
|---|---|---|---|
| tantalum, mg | niobium, mg | | |
| 4.00 | 3.5 | 2.62 | 3.96 |
| 4.00 | 7.0 | 2.65 | 4.00 |
| 7.92 | 7.0 | 5.24 | 7.91 |
| 7.92 | 14.0 | 5.30 | 8.00 |
| 15.80 | 7.0 | 10.44 | 15.76 |
| 15.80 | 14.0 | 10.50 | 15.86 |
| 30.30 | 14.0 | 20.20 | 30.50 |

In regard to the determination of tantalum and separating it from niobium, this communication must be considered preliminary.

It should be noted that the empiric formulae given above for the cerium, thorium and zirconium iodates obtained, can be used only for stoichiometric calculation, but they do not show the structure of these compounds. It may be assumed that the described compounds belong to the polyacid type, since cerium IV, thorium, and especially zirconium and tantalum are acid-forming elements. This partly accounts for the fact that cerium does not give sparingly soluble iodates, since the acid nature of an element increases with its valency. The presence of potassium in the resulting compounds may also be due to the assumed nature of these compounds, since polyacids are liable to give sparingly soluble salts with potassium, cesium and rubidium.

Rational formulae can be given to the above iodates only after they have been studied thoroughly.

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* The tantalum content was calculated, using the factor 1.51 (Table 1).

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*PHYSICAL CHEMISTRY*

# EFFECT OF ADSORBED SUBSTANCES—HARDNESS (OR STRENGTH) REDUCERS—ON THE MECHANICAL STRENGTH OF QUARTZ SEDIMENTS IN WATER

By P. REHBINDER, Corresponding Member of the Academy, and J. B. ARON

The decrease in strength of solids or in their hardness due to adsorption was found and studied in detail in this laboratory (1).

This phenomenon may be described in short as follows: changing the medium in which the destruction takes place, for instance, by introducing small admixtures of substances, called hardness reducers, which are adsorbed on the internal surface of the solid, greatly facilitates destruction processes, such as, for instance, processes of drilling in hard rocks. The rate of drilling can therefore be raised considerably by adding small quantities of hardness reducers to rinsing water (2). This is due to the surrounding medium (the liquid) penetrating into the « zone of predestruction», i. e. into the zone of microcracks which is developed under the action of external forces, sometimes to a considerable depth from the surface of the solid body. Thus, adsorption solvation layers are formed in the microcracks in the predestruction zone at the expense of the energy of wetting. These layers produce wedging forces in the cracks, analogous to the wedging action established by B. Derjaguin and co-workers (3).

To find out the mechanism of adsorption hardness reduction in drilling, it is of great interest to study the mechanical strength of «models» of cracked rocks, after soaking them in water or in aqueous solution of definite composition. In these experiments all the internal surfaces which open up in the solid in the course of its mechanical destruction, should be preliminarily coated with at least a very thin film of liquid.

Such models were made by compressing particles of the rock-forming mineral or rock of definite diameter precipitated in water, under the action of gravity, by free settling, or under the action of centrifugal force by centrifuging. Evidently, the mechanical strength of a sediment of the solid in the form of grains of definite diameter is determined by the thickness of the liquid films separating the grains, and increases sharply with the density of the sediment, i. e. as the thickness of the film decreases. Such sediments or dispersed masses when wetted with a liquid may have considerable shearing stress even if the particles are large. This phenomen is observed, for example, in wet sand. B. Derjaguin (4) was first to quantitatively establish rigidity in thin layers of water between glass surfaces. He found that the modulus of rigidity increases sharply as

the wetting film becomes thinner, and that rigidity already becomes manifest at thicknesses from 1—0.1 μ. It may be assumed, however, that when the liquid films are very thin, cohesion forces arise at the points of contact between the solid particles, which are the main factor for shearing stress in the sediments, as well as for the strength of coagulation structures, that form even in very dilute suspensions with drawn-out laminar particles (e. g. in colloidal clay suspensions in water, according to the works of N. N. Serb-Serbina in our laboratory). Thus, it may be considered that the mechanical strength of the sediments is analogous to the cohesive strength in separate aggregates which are formed by the suspension particles coagulating.

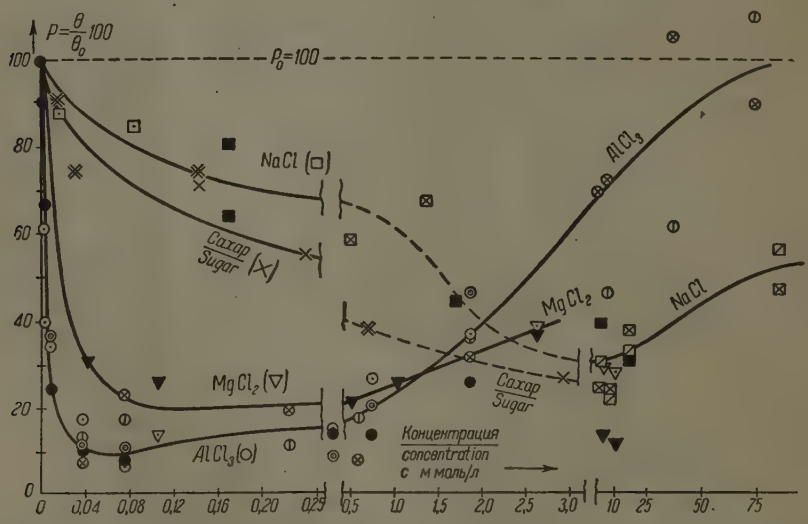
Sediments of various mechanical strength were formed in the same medium, time and forces of compression being varied by varying the rotation rate of the centrifugal apparatus. The strength of such sediments should be gauged by the greatest (critical) shearing stress which can arise in a volume of the sediments, when attained slowly enough. In measuring this critical stress the method applied was that of D. M. Tolstoi ([5]), which consists in measuring the slowly attained stress necessary to tear a cylindrical rod off of the medium whose strength is to be determined. The surface of the rod is covered with sharp screw threading in order to prevent gliding, i. e. in order to secure cohesion between the medium and the rod surface and to guarantee rupture near this surface, but inside the medium. In neutral and acid mediums aluminium rods with a diameter of approximately 2 mm were used, placed along the axis of a test-tube (with an inner diameter of approximately 10 mm) with the precipitate before densifying. The rod was easily entered without friction by means of a stopper with a metallic bushing. When the sediment densifies, the rod is caught in it. The test-tube with the sediment fastened to a stand was pulled downwards gradually by means of a micrometric screw; the rod was fastened to a vertical dynamometric spring (there was a set of such graduated springs for various stress intervals). As the spring gradually expanded, the greatest stress corresponding to the rod tearing abruptly off of the sediment was observed; this rupture was always «brittle» enough to give quite a definite strength value within rather large limits, independent of the rate of measuring. The critical shearing stress $P=\frac{F}{S}$ in g/cm² was calculated by dividing the force $F$ measured by the spring, by the lateral surface $S=\pi Dh$ of the submerged part of the rod, where $h$ is the length of the submerged part.

These experiments established quite a clear-cut decrease in the strength of the sediments when very small quantities of hardness reducers are added to the water in which a pure quartz sediment is formed. This considerably increases the rate of drilling in quartz rocks (quartzites) ([2]). The greatest effect in lowering the strength of the sediment (a decrease of 7—10 times in comparison to the same sediment in pure water) is attained in the concentration range, as has been established in laboratory and industrial experiments performed by workers of this laboratory, for the highest rate of drilling; for aluminium chloride this concentration range is from 0.01 to 0.1%.

To our regret, in spite of the constancy of all conditions being maintained and the limit density of the sediment in time being attained, these measurements give quite diverging values, especially for pure water. The values are most uniform, as might have been expected, where the concentration of the reducer in the water is optimal, giving the minimum strength of the

sediment. This circumstance was the cause of a great number of repeated measurements (for pure water this number was as high as 30—40), which made it possible to plot a curve showing the arrangement of a number of results according to their value, and to calculate from the maximum of this curve the most probable value of the critical shearing stress. When the number of repeated experiments was comparatively small, the most probable value was determined as the average of the most significant values, neglecting the most deviating ones. In almost all cases the average of all the measurements differs little from the most probable value, and in any case does not change the course of the relation between the sediment's strength and the concentration of the hardness reducer $P=f(c)$. It can be shown that in some cases irreproducibility is due to small differences in the volume decrease, i. e. in the densification of the sediment, and is compensated if these changes in volume are taken into account. The strength increases sharply even if the sediment is just a little more dense, and therefore it is difficult to avoid a certain scattering of values for $P$.

A relation has been established for sediments of pure quartz from rock-crystal between their mechanical strength and equilibrium concentrations of the following typical hardness reducers in aqueous solution: sodium, magnesium and aluminium chlorides, and sucrose (see Fig. and table).




Effect of hardness (or strength) reducers, electrolytes and sugar, on the mechanical strength of quartz sediments in aqueous solutions. For comparison the critical shearing stresses of $P=\frac{\theta}{\theta_0}\cdot 100$ are given in per cent of the initial value of $\theta_0$ in pure water; $AlCl_3$●, ⊗—polydispersed quartz, free settling; ○ — same, centrifuged; ⊙ — coarse quartz, free settling; ⊖ — same, centrifuged; $MgCl_2$ ▼ — polydispersed quartz, free settling; ▽ — same, centrifuged; NaCl ■ — polydispersed quartz, free settling; □, ⧄ — same, centrifuged; ⊠ — coarse quartz, centrifuged; $C_{12}H_{22}O_{11}$ × — polydispersed quartz, free settling; ※ same, centrifuged.

The study of coarse pulverized quartz (100—350 μ) was of special interest, since it could have been supposed for fine particles (below 10 μ) that changes in the strength of the sediment are entirely due to differences in packing as a result of various aggregation (coagulation) of the primary particles.

The data obtained show that the effect of hardness reduction on quartz

Effect of Adsorbed Substances on the Mechanical Strength of Quartz Sediments in Water [$C$—equilibrium percentage concentration; $\overline{P}$—critical shearing stress ($g \times cm^{-2}$), average of all values; $P_m$—ditto, most probable value; $n$—number of measurements]

I. Aluminium Chloride $AlCl_3$

| $C\%=0$ | $5.10^{-4}$ | $1.10^{-3}$ | $5.10^{-3}$ | 0.01 | 0.05 | 0.10 | 0.25 |
|---|---|---|---|---|---|---|---|

1. Fine polydispersed quartz $D=20$—$180\,\mu$, free settling (15 min.)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\overline{P}=327$ | 200 | 72 | 31 | 23 | 41 | 42 | (75) |
| $P_m=300$ | — | 70 | 30 | 24 | 40 | 40 | (75) |
| $n=34$ | 2 | 5 | 5 | 20 | 16 | 15 | 19 |

2. The same quartz centrifuged (15 min.)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $P_m=1360$ | 512 | 444 | 274 | 83 | 194 | 335 | 555—475 |

3. Coarse quartz $D=100$—$350\,\mu$, centrifuged (15 min.)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $C\%=0$ | 0.005 | 0.01 | 0.03 | 0.06 | 0.25 | 1 | 5 | 10 |
| $\overline{P}=724$ | 127 | 116 | 109 | 142 | 256 | 378 | (679) | 847 |
| $P_m=782$ | 101 | 134 | 85 | 133 | 277 | 360 | (500) | 863 |
| $n=19$ | 6 | 5 | 8 | 6 | 12 | 13 | 10 | 10 |

II. Magnesium Chloride $MgCl_2$

4. Fine polydispersed quartz, free settling

| | | | | | | |
|---|---|---|---|---|---|---|
| $C\%=0$ | 0.01 | 0.05 | 0.10 | 0.25 | 0.50 | 1.0 |
| $P_m=300$ | 75 | 63 | 76 | 110 | 40 | 35 |

III. Sodium Chloride NaCl

5. Fine polydispersed quartz, free settling

| | | | | | |
|---|---|---|---|---|---|
| $C\%=0$ | 0.01 | 0.05 | 0.10 | 0.25 | 1.0 |
| $P_m=300$ | 240 | 250 | 133 | 117 | 90 |

6. Coarse quartz, centrifuged

| | | | | | | |
|---|---|---|---|---|---|---|
| $C\%=0$ | 0.03 | 0.08 | 0.25 | 0.50 | 1.0 | 5.0 |
| $P_m=782$ | 460 | 500 | 185 | 184 | 294 | 367 |

IV. Sucrose

7. Fine polydispersed quartz, free settling

| | | | | | |
|---|---|---|---|---|---|
| $C\%=0$ | 0.01 | 0.05 | 0.10 | 0.50 | 1.0 |
| $P_m=300$ | (160) | 213 | 150 | 180 | 80—120 |

increases for electrolytes as the valency of the cation rises, i. e. as its hydratation increases (6) in the series: sodium, magnesium, aluminium. All the electrolytes show the same relation with the concentration, and give a well expressed strength minimum at low concentrations.

Preliminary studies by the authors showed that, irrespective of the form of the adsorption process, the mechanical strength of a sediment of primary coarse grains is in the same general relation to the concentration of the adsorbed and surface hydrating substance, as peptization of the aggregates (stabilization of fine particles), since these phenomena are due to the same cause—a change in the thickness of the liquid layer (solvate shell) which is connected with the surface of the dispersed particles. The abrupt decrease in strength found for these sediments by our measurements, is evidently due to the wetting liquid films between the quartz grains becoming thicker (at the thinnest points), which greatly decreases cohesion between the grains by decreasing the number of contacts between them. The works of B. Derjaguin's laboratory showed (3) that the adsorption monolayer greatly affects the thickness of the solvate films. This throws light upon a number of features of disperse systems which have been studied in our laboratory before (1). The thickest liquid film between the grains, i. e. the greatest looseness of the sediment under the adsorption action of a hardness reducer, corresponds to the least coagulation and to the minimum on the strength curve $P=f(c)$.

Further increase in the concentration of the electrolytes always leads to a decrease in the thickness of the diffused double layer, and consequently, of the film, which results in greater coagulation and higher strength $P$.

These measurements may be of use in the future for a rational choice of optimal hardness reducers and their concentrations for typical rocks and rock-forming minerals. Besides this, it has been shown that admixtures of hardness reducers may be applied for abrupt decreases in the strength of sediments (loosening), for instance, those that form in pit-holes when the instrument gets «caught».

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*GEOCHEMISTRY*

# POSSIBLE TYPE OF CASSITERITE MINERALIZATION IN THE NEAR-POLAR URALS

By S. G. SARKISIAN

*(Communicated by A. E. Fersman, Member of the Academy, 15. VII. 1940)*

In order to organize properly the search for primary cassiterite deposits, it is necessary to establish the possible type of tin mineralization. This may be done in two ways: the first is to study the character of granitoids in order to find out the characteristical features, inherent in stanniferous varieties only; it should be noted that the fact alone of their being stanniferous does not point to a definite type of primary mineralization, not to speak of the fact that this feature is highly variable and applicable only to certain regions or areas.

An investigation of this type will yield no results until a detailed analysis of the material (microscopic, spectroscopic and chemical) is performed. The problem of tin being one of the most actual at the present moment, a way ought to be chosen that would yield immediate results. And this is the study of paragenetic mineral associations in loose deposits; a record of some or other minerals accompanying cassiterite, be it in eluvium, friable deposits or alluvium, suggests the possibility of the presence of a definite type of tin mineralization in areas of feeding. Aside from this, the character of association of the minerals accompanying cassiterite in loose deposits, in accordance with the geomorphology, and the general geological structure of the country, points to the possible degree of cassiterite concentration in loose deposits, i. e. the possibility of alluvial deposit formation.

In the summer of 1939 the author made mineralogical investigations of the loose sediments in the Naroda, Manj-ya and Shchokur-ya river basins. This work was taken up in connexion with the fact of cassiterite grains having been found by N. A. Sirin in the alluvium of the above rivers. Different types of loose sediments were studied, viz., alluvial (recent and ancient), moraine, eluvial and friable deposits, lacustrine and aeolian.

Of the loose sediments most widely spread are alluvial deposits, which present partly a product of out-wash of moraine formations. Most interesting from the standpoint of a search for primary mineralization is the alluvium presenting a product of erosion of primary rocks only. Such a type of alluvium is to be found chiefly in small tributaries, while in large rivers a redeposition of loose formations of various types takes place, the hereditary features of the sediments are smoothed away, the useful minerals become disseminated and paragenetic associations can be established with difficulty.

The loose sedimentary deposits of the near-polar Urals are chiefly represented by coarse clastic material. The finer portion consists of coarse-grained and less frequently of fine-grained sand. Argillaceous material is scarce.

The mineralogical composition of the loose material is as follows: gold, sphalerite, galena, molybdenite, pyrrhotite, bornite, chalcopyrite, pyrite, arsenopyrite, quartz, corundum, haematite, rutile, cassiterite, zircon, thorite, anatase, brookite, limonite, calcite, scheelite, magnetite, chromite, apatite, monazite, augite, diopside, common hornblende, disthene, topaz, garnet (chiefly almandine, also pyrope, spessartite), feldspars (orthoclase, less frequently plagioclase), epidote, orthite, muscovite, biotite, chlorite, tourmaline, titanite, ilmenite.

Thus, of useful minerals, gold, scheelite and cassiterite are encountered here. Cassiterite is found in the form of small grains (0.1—0.5 mm) of a brown colour, lustre greasy or metallic, fracture uneven to semi-conchoidal; usually angular grains, sometimes with well preserved crystallographic forms, prisms and pyramids.

Cassiterite in loose deposits is accompanied with sulphides (pyrite, chalcopyrite, arsenopyrite). Cassiterite is sometimes encountered in intergrowth with sulphides; this shows that the above-mentioned associated minerals are not accidental, but have a paragenetic relationship with cassiterite.

Thus, it may be assumed that the formation of cassiterite-bearing loose deposits is connected with the decay of the primary tin mineralization of the sulphide type.

Our prognosis is upheld by findings at the western slope of the Urals in the Torgovaya river basin of quartz-sulphide veins with fine grains of brown cassiterite with a habit strikingly similar to that of cassiterite grains found by the author at the eastern slope of the Urals, in the investigated river basins, chiefly in the creeks Bolshaya and Malaya Lyapto-Yakha (the Naroda river basin).

Hence the necessity of a thorough investigation of the sulphide veins of the near-polar Urals as a possible cassiterite holders.

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# CHLORINE AND BROMINE IN MASSIVE CRYSTALLINE ROCKS

By L. S. SELIVANOV

*(Communicated by W. I. Vernadsky, Member of the Academy, 10. VI. 1940)*

This paper gives the first results obtained by us in a study of the chlorine and bromine content in massive rocks. A part of our methodical work on determining small quantities of bromine has already been published (1). Additional special data on the analysis of rocks will be given in a separate paper: only the most essential data are given here.

A weighed portion of 1—1.5 g of rock was fused with 5—6 times as much KOH, and the melt was treated with hot water; then the solution was filtered, the filtrate saturated with $CO_2$, evaporated to dryness and extracted with alcohol. Bromine was determined in the extract iodometrically in the form of $BrO_3^-$ after our modification of J. van der Meulen's method. In this manner as small a quantity as $2—4\times10^{-7}$ g of bromine can be determined quantitatively. Control experiments, in which known quantities of bromine (in the form of KBr) were added to the rock, showed a certain tendency to loss in the bromine added, analogous to that observed sometimes in determining iodine. This loss averaged 15—18% of all the bromine added. Thus, the error of each determination amounted to $(0.2—0.4)\times10^{-4}$% Br for the above sample, the found quantity of bromine being possibly systematically lower than the true quantity. All the data given below are averages of two separate, well coinciding results. In preparing the material for analysis care was always taken that no tainted or weathered parts of the rock fall into the test sample.

The data obtained on the gross chlorine and bromine content in rocks are given in Table 1.

Table 2 gives the averages for separate types of rocks, for which several (two or more) determinations were made. In finding the average chlorine and bromine contents in rocks, data on the mineral dashkesanite were excluded for evident reasons; besides, this mineral differs pronouncedly from the rocks in its chlorine content. Thus:

1. The mean arithmetical bromine content in the 23 studied rocks equals $1.62\times10^{-4}$%, the mean arithmetical chlorine content being $3.14\times10^{-2}$%.

2. The separate types of rocks differ very little in their chlorine and bromine contents. Some regularity becomes evident only if the rocks are arranged in order of decreasing acidity. In such a case, the most acid and most basic rocks contain somewhat less bromine than the intermediate rocks.

Table 1

| Rocks | Location | Cl, % | Br, % | Cl/Br |
|---|---|---|---|---|
| Hypersthen rock | Anabara r., Yakut, ASSR | $2.5\times10^{-2}$ | $8.3\times10^{-5}$ | 301 |
| Alkaline granite | Iinpor | $0.9\times10^{-2}$ | $2.0\times10^{-4}$ | 45 |
| Granite | Urals, st. Berdyaush | $3.7\times10^{-2}$ | $1.7\times10^{-4}$ | 218 |
| Granodiorite | North Karelia, Ukhta district | $3.0\times10^{-2}$ | $7.4\times10^{-5}$ | 405 |
| Hybrid rock | Onéga lake | $1.9\times10^{-2}$ | $1.7\times10^{-4}$ | 112 |
| Quartz syenite | Omolon r. | $0.1\times10^{-2}$ | $2.9\times10^{-5}$ | 34 |
| Granite | Katun Alps, Altai | $4.0\times10^{-2}$ | $2.5\times10^{-4}$ | 160 |
| Granodiorite (hornblende) | Topozero, massif Kuevara | $7.9\times10^{-2}$ | $4.4\times10^{-4}$ | 180 |
| Biotite granite | Katun Alps, Altai | $2.4\times10^{-2}$ | $1.1\times10^{-4}$ | 171 |
| Biotite-hornblende, schlier in granite | Daryal, Caucasus | $5.3\times10^{-2}$ | $6.8\times10^{-5}$ | 780 |
| Chlorite banatite | Sadon canyon, Central Caucasus | $2.4\times10^{-2}$ | $6.5\times10^{-5}$ | 369 |
| Syenite | Abkhasia | $9.8\times10^{-2}$ | $1.7\times10^{-4}$ | 577 |
| Andalusite hornstone | New-Siberian isl. | $3.0\times10^{-2}$ | $9.7\times10^{-5}$ | 309 |
| Biotite-nepheline syenite | Vuonnemyok basin | $2.4\times10^{-2}$ | $1.0\times10^{-4}$ | 240 |
| Syenite-diorite | Lake Gokcha | $3.7\times10^{-2}$ | $1.3\times10^{-4}$ | 285 |
| Sodalite foyaite with eudialyte | M. Puankaruaiv | $2.8\times10^{-2}$ | $2.3\times10^{-4}$ | 122 |
| Basalt | Great Vilui lake, Kamchatka | $4.6\times10^{-2}$ | $4.6\times10^{-4}$ | 100 |
| Gabbro-diabase | Neighbourhood of Borjom, Caucasus | $1.4\times10^{-2}$ | $1.2\times10^{-4}$ | 117 |
| Basalt of porphyritic structure | Adjaristan | $1.2\times10^{-2}$ | $2.6\times10^{-4}$ | 46 |
| Gabbro | North-west Altai | $2.6\times10^{-2}$ | $2.8\times10^{-4}$ | 93 |
| Teshenite | Barnet | $1.5\times10^{-2}$ | $5.0\times10^{-5}$ | 300 |
| Feldsparred ijolite | Tury cape | $3.1\times10^{-2}$ | $9.7\times10^{-5}$ | 320 |
| Melilite basalt | Tury cape | $2.0\times10^{-2}$ | $8.1\times10^{-5}$ | 247 |
| Dashkesanite * | Dashkesan deposit, Az. SSR | 3.25 | $2.9\times10^{-4}$ | 11 200 |

Table 2

| Rocks | Number of samples | Average | | |
|---|---|---|---|---|
| | | Cl, % | Br, % | Cl/Br |
| Granites | 5 | $3.3\times10^{-2}$ | $1.60\times10^{-4}$ | 275 |
| Granodiorites | 2 | $5.4\times10^{-2}$ | $2.57\times10^{-4}$ | 292 |
| Syenites | 4 | $4.0\times10^{-2}$ | $1.07\times10^{-4}$ | 284 |
| Gabbros | 2 | $2.0\times10^{-2}$ | $2.00\times10^{-4}$ | 105 |
| Basalts | 3 | $2.6\times10^{-2}$ | $2.67\times10^{-4}$ | 131 |
| Average of all rocks studied | 23 | $3.14\times10^{-2}$ | $1.62\times10^{-4}$ | 243 |

3. The ratio Cl/Br varies widely and averages 243.

This ratio is noticeably lower for basic than for acid rocks (Cl/Br—from 46 to 320; average value—198).

* For description of dashkesanite (the only mineral studied by us) and its composition see paper by G. A. Krutov [2].

Besides rocks, several meteorite samples were analyzed for chlorine and bromine content; the values obtained for them were of the same order as for the rocks. Data on the «Saratov» meteorite were published by us not long ago ([3]).

Let us analyze our results. The first and only experimental data on bromine content in rocks and minerals belong to Th. Fellenberg and G. Lunde ([4], [5]). The ten figures found by them range from $2\times10^{-4}$ to $2\times10^{-3}$% of Br (average $6.4\times10^{-4}$% Br). Ignoring those cases in which bromine was not found at all, owing to the poor sensitivity of the method, almost all these values are considerably higher than ours. In evaluating these data it must, however, be taken into account that all the figures for bromine were obtained after an unchecked method of low sensitivity; besides, the authors did not have at hand sufficiently pure reagents.

The average bromine content was obtained by us without taking into account the relative distribution of the rocks studied. However, the necessary correction would change our value very little, since rocks of various types differ little on the average in their bromine content. In particular, the most common granites and granodiorites in the earth's crust contain on the average $2.07\times10^{-4}$% Br. The supposed (not experimental) bromine contents in massive rocks and meteorites differed in most cases very greatly (tens and hundreds of times) from the actual concentration found by us [data for rocks, see F. Clarke and H. Washington ([6])]. The rocks studied by us contained an average of $3.14\times10^{-2}$% Cl. This value is within the limits of chlorine concentration in igneous rocks, given by various authors ([6]). In this paper we shall not go into an analysis of these average chlorine content.

In one of our previous papers ([7]) we dwelt on the fact that bromine concentrates in soils, peats and other formations, in whose origin organisms play an important part. It was then found that soils contain an average of $6.51\times10^{-4}$% and peats $3.10\times10^{-3}$% Br. Having now on hand data on the content of bromine in rocks, we are in a position to build a quantitative idea as to the degree of this concentration. The bromine content in soils is at least four, and in peats—at least twenty times as great as that in rocks. Almost all of this bromine is in union with the organic substances in soils, peats, etc., and its quantity on the whole earth's surface is probably about $10^7$—$10^8$ tons [for the carbon content in soils, etc., see Waksman ([8])], not counting the bromine of the skeleton part of soils, etc. Without doubt, this accumulation of bromine is of great importance in all the history of its atoms in the biosphere. The greater part of the rocks studied (15 out of 23) have a low ratio Cl/Br ($<293$); as has been mentioned, the average ratio is 243. This value is considerably lower than the corresponding ratio for the ocean (293).

Chlorine, as we know, is easily, but not completely washed out of the weathering products of igneous rocks, and is carried into the sea together with river waters. Together with a number of other elements, bromine to some extent shares the same fate. In studying the value of the ratio Cl/Br for the sea and for igneous rocks, we come to a conclusion that: 1) either part of the bromine accompanying the chlorine on its way from the rocks to the sea is held up somewhere, or 2) the sea has (or had) some separate source of chlorine which is poor in bromine. Either of these processes or a definite combination of both of them could have had the same result, viz., increase in the ratio Cl/Br in sea water in comparison to rocks.

We have already mentioned the accumulation of bromine in soils and peats (the chlorine content in them is the same as in rocks, i. e. $n\cdot10^{-2}$%). This cannot, however, explain the difference in ratios under discussion,

since in this case we are dealing with a lack of bromine in the sea of the order of $n \cdot 10^{-14}$ tons. The lacking bromine could hardly be sought in sedimentary rocks either, since in such a case they should contain $n \cdot 10^{-2}\%$ Br. Although the bromine content of the most common types of sedimentary rocks has not yet been studied by anybody, the upper limit of its content in them can be judged from the data of Krejci-Graf and Th. Leipert ([18]), who having studied the bromine content in a number of rocks containing a great quantity of organic matter (sapropelites etc.), usually found $n \cdot 10^{-3}$ or even $n \cdot 10^{-4}\%$ Br in them. Thus, our first assumption is not confirmed, and besides it is based on the supposition that the salt content of the ocean has its origin in the salt borne down by rivers.

However, quite a while ago there appeared another viewpoint on this matter, which sought the source of the ocean's salt content in the volcanic phenomena—see, for instance, W. I. Vernadsky «The History of the Minerals of the Earth's Crust» (vol. 2, 3rd ed., 1936). V. Goldschmidt ([9], [20]) gives some quantitative calculations on the basis of this viewpoint. He considers that the quantity of chlorine and certain other elements occurring in the sea is considerably greater than that which could be contained in weathered igneous rocks. In another paper ([19]) Goldschmidt points out a whole group of elements, including Cl, Br, I, which could come out onto the earth's surface mainly as gases, or together with hydrothermal solutions. Goldschmidt calls them the «Entgasungsprodukte» of the lithosphere. The difference in the ratio Cl/Br for the sea and for massive rocks could be due in this case to the singular content of both haloids in these products. Such an enrichment exists at present in the form of volcanic exhalations, many of which contain $Cl_2$, HCl and a number of solid chlorides ($NH_4$, Fe, etc.). See, for instance, a summary of some of the papers on this problem, compiled by Beloussov ([10]). In some cases there are even quantitative calculations of t e chlorine carried out into the atmosphere and finally into the sea ([11]); according to the data of many other papers, such calculations can be made [in particular, see J. Stoklasa's paper ([12])].

Besides chlorine and fluorine, volcanic gases contain iodine ([13]) and bromine [see observations made by R. Matteucci during the eruption of Vesuvius ([14], [15])]. Bromine has also been found more than once by various authors in volcanic sublimates—in halite, sylvite and lawrencite, where it was sometimes determined quantitatively [for summary of data on this problem see F. Zambonini ([16]) and also O. Deines ([17])]. In several cases the data given make it possible to deduce the ratio Cl/Br which is of great interest, in view of the above, and which in such products is evidently over 300. However, there are no special determinations of this value at all, although there is no difficulty in making them (e. g. in the Soviet Union from the materials on Klutchevsky volcano).

Without suggesting premature solution to the question under discussion, we shall mention only that the paths of chlorine and bromine may diverge in this case just as in many others. From this viewpoint, of particular interest are the results of an analysis of the scarn mineral dashkesanite which contains only $2.9 \times 10^{-4}\%$ of Br and a large quantity of chlorine—3.25%. This is an example of such a separation in the paths of migration of both haloides, which is perhaps of more general than accidental nature.

In concluding we wish to express our deep gratitude to W. I. Vernadsky and A. P. Vinogradov for a number of valuable instructions and B. M. Kupletsky for material kindly placed by him at our disposal.

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# DISTRIBUTION OF METAL VALUES IN ORE DEPOSITS

By N. K. RAZUMOVSKY

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In investigating the distribution of gold grains in placers as to size and weight, it was ascertained that the logarithms of weight (or mean diameter) are distributed according to size classes with frequencies determinable by the equation of Hauss:

$$y = \frac{W}{\sigma\sqrt{2\pi}} e^{-\frac{(x-M)^2}{2\sigma^2}} \qquad (1)$$

where $y$ is frequency, $W$—total weight of gold grains, $x$—logarithm of weight of individual granules or of the mean weight of a gold grain of a class ([4]). Concomitantly with this investigation, the distribution of gold content (irrespective of grain size) was also subjected to analysis from samples taken out of test-pits sunk in a great number of spots all over the area of the gold-bearing layer relieved from the overlying burden. It was found that in this case, too, the logarithms of contents (i. e. of weight per unit volume) were distributed normally, according to the law of Hauss. This fact appeared to be of particular interest in two respects: first, it proved that chance sampling fails to give a symmetrical distribution even under limiting conditions. Indeed, under the conditions of the given investigation when the testpits were distributed over the gold-bearing layer in a checkered arrangement, we evidently kept to the conditions of chance sampling. But the experience showed a sharply asymmetrical distribution of samples failing to obey Hauss' law, as might have been expected from the nature of chance samplings.

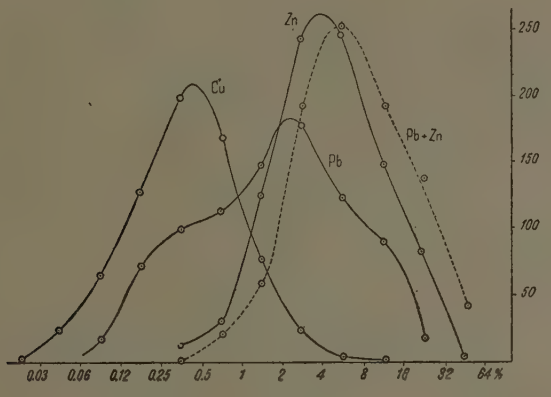
Secondly, the distribution of contents according to a normal logarithmical law, induced the author to surmise that the appearance of this law of distribution is not only associated with the laws of hydraulics, but also with some deeper lying physical causes. With this idea in mind, the author set about to search for a really rich material of samplings of ore deposits. Thanks to the kindness of Kurek, Chief Geologist of the Scientific Research Geological Prospecting Institute, he was afforded the possibility to investigate about a thousand analyses of copper, lead and zinc ores from 4th level of the Novo-Sokol lens of the Ridder deposit. The logarithmical normal law was found to be predominant in this case too, this being true both for the contents of metals taken separately and for sums, as for instance for Pb+Zn.

From the properties of the logarithms it is obvious that equidistanced classes in logarithms will give a geometrical progression of contents. Accordingly, the simplest way for bringing out logarithmically normal law is to set up classes in a geometrical progression with twofold increase, for instance, and then to find the frequencies for these classes. Resorting to ordinary methods, we next verify how close these frequencies are following Hauss' law. The table gives unmistakable evidence that in the case under conside-

ration this law holds true for all the investigated components*. For copper the mean in logarithms is 1.576 (0.377% Cu) and $\sigma = 0.427$. In column 2 are given the theoretical frequencies, calculated according to the law of Hauss. They are seen to stand sufficiently close to the empiric frequencies.

| Fraction, % | Number of analyses | | | | Fraction, % | Number of analyses | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cu | Pb | Zn | Pb+Zn | | Cu | Pb | Zn | Pb+Zn |
| 0 | 67 | 54 | 59 | 58 | 1— 2 | 76 (79) | 148 | 125 | 59 |
| Traces | 161 | 16 | 1 | — | 2— 4 | 24 (25) | 178 | 242 | 192 |
| 0.01—0.03 | 2 ( 3) | 0 | — | — | 4— 8 | 2 ( 5) | 123 | 247 | 249 |
| 0.03—0.06 | 25 ( 19) | 1 | — | — | 8—16 | 1 ( 1) | 91 | 138 | 190 |
| 0.06—0.12 | 65 ( 67) | 9 | — | — | 16—32 | — | 19 | 83 | 129 |
| 0.12—0.25 | 127 (142) | 36 | — | — | 32—64 | — | — | 1 | 42 |
| 0.25—0.50 | 198 (190) | 100 | 13 | 1 | $M =$ | 0.576 | 0.272 | 0.620 | 0.804 |
| 0.50—1.00 | 168 (157) | 111 | 33 | 21 | $\%_0 =$ | 0.38 | 1.87 | 4.17 | 6.37 |
| | | | | | $\sigma =$ | 0.427 | 0.544 | 0.419 | 0.413 |

In another case the author found the distribution of the geometrical parameters of ore bodies, and in particular of the thicknesses obtained in sampling, to follow the normal logarithmical law too. The reason for this circumstance is not clear, however. It may possibly lie in the fact that we have here to deal with spatially dependent magnitudes rather than a discrete distribu-




tion, as is mostly the case in statistical study. Indeed, two samples, not far apart from each other, will be also near in their contents, and with the distance approaching to zero, the samples tend to equality. Thus, we deal here with the testing of mutually connected magnitudes, and it is probably this circumstance which is responsible for the appearance of this peculiar «logarithmically normal» law. This law is, to all appearances, the most asymmetrical among all the distribution laws actually available in nature.

From all the above-stated, conclusions important both for the theory and practice may be drawn: 1. The arithmetical mean from ore samplings

* Since the components are given in %, the doubling of classes may be extended up to 50% of the substance obtained [besides this, we have, strictly speaking, not Pb, but PbS (87% Pb), and not Zn, but ZnS (60% Zn); it is therefore necessary for a 50% mineral to have 44% Pb and 30% Zn]. Further, the substance is to be considered as a solvent, and all the rest as «contents» which should be twice reduced. However, for our case this circumstance is of no consequence, and its ignoring on our part did not prevent us from bringing out the respective maxima, as well as the symmetry of distribution.

fails to be the best mean and only very roughly characterizes the deposit. A more proper value is the geometrical mean. 2. The methods used for computation of available reserves in ore and placer deposits should be changed, so as to take due account of the existence of the logarithmically normal law. 3. The logarithmically normal law appears to be far more widely spread in nature than it was hitherto believed. Thus, this law governs the distribution of suspended particles in water and in air; of the particles of various rocks obtained in grinding; the distribution in chemical precipitation and sieve analysis; the distribution of valuable rock components including oil and perhaps the constituent minerals of rocks in general.

As this law underlies the distribution of particles in a sediment, it can also be supposed to play a certain rôle in molecular physics. All that has been stated here calls for great attention to the study of this law.

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*BIOCHEMISTRY*

# WHAT CONDITION IS RUBBER IN PLANTS

By A. A. PROKOFIEV

*(Communicated by A. A. Richter, Member of the Academy, 18. IV. 1940)*

All rubber plants of this country can be divided into two groups according to the degree of polymerization and the conditions of formation of their rubber.

To the first belong those (guaula) forming their rubber in their parenchymal tissues where it is stored up along with very considerable amounts of resinous substances ([7]). The rubber and resin are united here into a homogeneous mass, which is a solution of the former in the latter*. A feature distinctive of the rubber thus formed is its low degree of polymerization—its low molecular weight. The plants of the second group (tau-saguyz, kok-saguyz, krym-saguyz) form their rubber in their lacteal system. This rubber is in a state of high polymerization, has a high molecular weight**. Resinous substances are poor in the lacteals of saguyz plants.

As the lacteal tube grows, its rubber particles increase in size until a certain limit is reached. Those in tau-saguyz and krym-saguyz, which are tiny globules at the start of this process, become at its end slightly curved rods, 10—12 cm long ([1,2]). The lacteal tube dies away at a definite age and its contents coagulate to form a thread consisting largely of rubber.

These changes in the condition of the rubber affect its physicial and chemical properties, its solubility in particular.

It has long been known that along with the fraction soluble in benzene and ether an insoluble fraction is contained in the rubber from the latex of some tropical plants ([10—12] and others).

The formation of the insoluble β-rubber out of the soluble α-rubber has been interpreted by several different workers as a transition of the linear thread-like molecules of the latter into the three-dimensional macromolecules of the former. The effect of benzene or ether upon β-rubber is only to swell it somewhat, without dissolving ([3,9]). In face of this evidence no attempt appears to have been made as yet to estimate the insoluble fraction in vegetable analyses for rubber, but the standard method used in such cases has been rather to extract the rubber by solvents, whereby the soluble fraction alone can possibly have been detected.

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* A drop of this homogeneous mass from the cells of guaula is a mixture of rubber, resin and essential oil ([6]).

* Its high degree of polymerization in saguyz plants has been established by Ignatiev ([4]) and Mashtakov ([5]) viscosimetrically.

Meanwhile our observations of 1939 have shown some plants to be notably high in that insoluble fraction at certain periods of their life. So is the kok-saguyz, for instance, whose cap tissues while dying away are consisting largely of β-rubber.

When thin small slices of vegetable tissue from the root of kok-saguyz are treated first with alcohol (for dehydration) and then with chloroform or benzene (to extract the rubber), the major part of the rubber contained in the root cap will not leave the slice tissue even after 12 hours of extraction with boiling solvent*. That rubber is present in the slices after extraction can be stated by bromination (⁸). It may be remarked here that the transition of rubber in an insoluble condition is also favoured by the dying away of the lacteal tube, for this results in coagulation of its contents into a rubber thread.

By analyzing the cap enveloped roots of kok-saguyz, it has been established that about 20% of their total content of rubber is taken up by the insoluble fraction. It will be obvious that a two-year-old kok-saguyz which has its roots capped (i. e. part of their tissue died off) is actually much higher in rubber, than it would appear from a number of analyses carried on according to the standard method during the foregoing years. A representative illustration to this is furnished by the data obtained by O. J. Sobolevskaya in analyzing the kok-saguyz roots according to our indications (see table).

Content of Insoluble Rubber in Kok-Saguyz Roots

| Experimental material | Content of rubber as determined | | % of insoluble fraction in the total rubber | Content of resin as determined | |
|---|---|---|---|---|---|
| | by the standard method | with taking the insoluble fraction into account | | by the standard method | with taking the insoluble fraction into account |
| Capped roots of a 2-year-old kok-saguyz (sampling May 16) . . . . . | 9.60 | 11.60 | 17.3 | 2.46 | 3.32 |
| Roots of an one-year-old kok-saguyz (sampling Oct. 15) | 7.63 | 7.60 | 0.0 | 3.02 | 2.96 |

The capped roots of a two-year-old kok-saguyz are seen in the table to have their ratio of the insoluble to the soluble rubber as 17.3 to 82.7. The insoluble fraction appears to have arisen from the rubber having changed its condition in the died off lacteals of the cap, for no such fraction was available in the roots of one-year-old plants, where the dying away of lacteals had practically not taken place. These results compel us to modify the usual method of rubber estimation so as to make it possible to determine the total rubber, whatever its condition may be in the plant.

The most simple way toward that purpose is this. When the roots of kok-saguyz are ground, the main quantity of rubber separates in the form of «worms». What remains is very poor in rubber. By rolling these worms during 25—30 min. one may turn their β-rubber into soluble state. Oxidizing destruction of rubber takes place in this process according to Staudinger (⁹).

* The standard method for rubber estimation is to treat the material with a boiling benzene or chloroform during 3 hours only.

The products arising from the destruction of three-dimensional molecules are easily soluble in chloroform and benzene, and it is not a difficult matter to determine them in the usual way.

The possibility of insoluble rubber being formed must be taken also into account in the experiments on plant starvation. When part of their soluble rubber has disappeared from the starving plants, this does not necessarily mean that some rubber has been actually lost; it may merely have been converted into another condition.

The established increase in β-rubber after dying away of lacteals suggests a revision of available data on rubber content for those perennial plants which contain rubber not only in the latex, but also in the form of threads (tau-saguyz, kok-saguyz, krym-saguyz).

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*BIOCHEMIE*

# GRAD DER WASSERSÄTTIGUNG ALS FAKTOR DER REGULIERUNG DER WIRKUNGSRICHTUNG DER INVERTASE IN DEN PFLANZEN

Von N. SISSAKIAN und A. KOBIAKOVA

*(Vorgelegt von A. N. Bach, Mitglied der Akademie, den 10. IV. 1940)*

Gegenwärtig ist schon genügend experimentelles Material vorhanden, welches für den engen Zusammenhang zwischen dem Wassergehalt der lebenden Pflanzenzelle und der Umkehrbarkeit der Wirkung einer Reihe von intrazellulären Fermenten spricht. Die Deprimierung der synthetisierenden Wirkung der Invertase und die Zunahme ihrer hydrolytischen Fähigkeit wurde zuerst von Kursanov [1] an Theeblättern gezeigt. Diese Annahme fand dann eine weitere Entwicklung und eine gründliche experimentelle Bestätigung durch die Untersuchungen von Sissakian [2,3] über die Invertase, Sissakian und Kobiakova [4,5,6] über die Proteasen und Phosphotasen. Diese Untersuchungen waren jedoch gewissermassen einseitig, da durch sie nur der Einfluss der ungenügenden Feuchtigkeit auf die umkehrbare Aktivität der Fermente aufgeklärt wurde, während der Einfluss der vollen Wassersättigung der Pflanzengewebe auf die Umkehrbarkeit der Fermentreaktionen in den Pflanzen unerforscht blieb. Diese Untersuchungen haben indessen nicht nur ein theoretisches Interesse, sondern sie können gleichzeitig auch eine angewandte Bedeutung bei der Schaffung einer rationellen Theorie des Hydromoduls der Pflanze bekommen. Die vorliegende Untersuchung wurde daher zur Feststellung des Zusammenhanges zwischen dem Grade der Wassersättigung und der Wirkungsrichtung der Invertase vorgenommen. Die Blattspreiten 10-tägiger Keimpflanzen zweier Weizensorten («Markis» und *Lutescens* 062) wurden mit Wasser gesättigt durch Eintauchen in dasselbe während 40 Min. Danach wurde durch schnelles Entfernen eines Teiles des Wassers durch Föhn ein differenzierter Wasserdefizit hergestellt. Nach einer Stunde wurden Pflanzenproben zur Bestimmung der synthetisierenden und hydrolysierenden Wirkung der Invertase nach der Methode von Kursanov [7] der Infiltration unterworfen. Die Ergebnisse der Versuche mit der Sorte *Lutescens* 062 sind in der Tabelle 1 dargestellt.

Tabelle 1 zeigt, wie wesentlich der Wassergehalt der Zelle die synthetisierende und hydrolysierende Aktivität der Invertase beeinflusst. Eine hohe fermentative Aktivität entwickelt die Pflanzenzelle bei natürlichem Wassergehalt, welcher im vorliegenden Falle 86.8% entspricht. Wir finden dabei nicht nur eine hohe Aktivität der Synthese sowie auch der Hydrolyse, sondern auch das günstigste Verhältnis zwischen ihnen. Die starke Sättigung der Zelle mit Wasser sistiert die Synthese vollständig. Der Verlust der Pflanze an Wasser bei natürlichem Wassergehalt der letzteren führt zur Abnahme der synthetisierenden Fähigkeit der Invertase. Die Hydrolyse erleidet dabei keine wesentlichen Veränderungen. Infolge der einseitigen Abnahme der synthetisierenden Wirkung verschiebt sich das Fermentgleichgewicht bei dem sich verstärkenden Wasserdefizit zu Gunsten der Hydrolyse.

Tabelle 1

Wirkungsrichtung der Invertase in Abhängigkeit von dem Grade des Wasserreichtums der Pflanzenzelle

| Wassergehalt der Blattspreiten in % | Wirkung der Invertase | | Verhältnis $\frac{S}{H}$ | Anmerkung |
|---|---|---|---|---|
| | Synthese S | Hydrolyse H | | |
| 90.6 | 0.0 | 12.6 | 0.00 | |
| 86.8 | 5.4 | 14.4 | 0.37 | Natürlicher Wassergehalt des Blattes |
| 78.6 | 2.6 | 10.0 | 0.26 | |
| 68.6 | 3.0 | 14.0 | 0.21 | |
| 58.6 | 2.7 | 12.6 | 0.21 | |
| 48.6 | 2.6 | 14.0 | 0.18 | |
| 38.6 | 1.2 | 12.8 | 0.09 | |

Tabelle 2

Wirkungsrichtung der Invertase in Abhängigkeit von dem Grade des Wasserreichtums der Pflanzenzelle

| Wassergehalt der Blattspreiten in % | Wirkung der Invertase | | Verhältnis $\frac{S}{H}$ | Anmerkung |
|---|---|---|---|---|
| | Synthese S | Hydrolyse H | | |
| 90.8 | 0.6 | 2.5 | 0.24 | |
| 83.4 | 9.5 | 1.2 | 7.92 | Natürlicher Wassergehalt des Blattes |
| 73.8 | 3.1 | 2.5 | 1.24 | |
| 63.8 | 3.1 | 2.8 | 1.11 | |
| 53.8 | 0.8 | 1.8 | 0.44 | |
| 43.8 | 0.0 | 1.6 | 0.00 | |
| 33.3 | 0.0 | 3.8 | 0.00 | |

Die an Keimpflanzen des Weizens *Lutescens* 062 festgestellte Abhängigkeit der fermentativen Synthese und Hydrolyse von dem Grade des Wasserreichtums der Pflanzengewebe hat sich auch für die Blattspreiten der Keimpflanzen der Weizensorte «Markis» als richtig erwiesen (Tab. 2).

Eine Deprimierung der Synthese, wenn auch in geringerem Grade, wird auch bei Wasserdefizit beobachtet. Wiederholte Untersuchungen der Abhängigkeit der fermentativen Aktivität der Zelle von ihrem Wasserregime, die an denselben Weizensorten ausgeführt wurden, ergaben dieselben Resultate.

Wir wenden uns jetzt zu den Abbildungen 1 und 2.

Die Kurven zeigen, dass wir bei der nichtdürreresistenten Sorte «Markis» ein auffallendes Vorherrschen der Synthese über die Hydrolyse in den Grenzen des Wassergehaltes der Zellen von 83.4—63.8% vorfinden. Bei demselben Wassergehalt ist bei *Lutescens* 062 das Gleichgewicht zu Gunsten der Hydrolyse verschoben. Überall überwiegt die Hydrolyse die Synthese. Jedoch der Vergleich der Kurven der Synthese mit denen der Hydrolyse weist bei diesen Sorten sehr wesentlichen Unterschied in der Wirkungsrichtung der Invertase auf. Die dürreresistente Sorte *Lutescens* 062 hat ein stabileres fermentatives System mit kleinerem Verhältnis der Synthese zur Hydrolyse. Diese Stabilität kommt beim Auftreten eines starken Wasserdefizites zur Geltung. Der fermentative Apparat bei der nichtdürreresistenten Sorte «Markis» ist labiler mit deutlichem Vorherrschen der Synthese über die Hydrolyse. Diese Labilität äussert sich in starker Abnahme der synthetisierenden Aktivität bei verhältnismässig geringem Wasserdefizit. Bei der Sorte «Markis» führt ein geringerer Wasserdefizit als bei *Lutescens* 062 zum volkommenen Sistieren der Synthese.

Wesentlich ist hier jedoch der Umstand, dass eine Erhöhung des Wassergehaltes der Zelle über die Norm, welche im vorliegenden Fall für *Lutescens* 062—90.6% und für die Sorte «Markis»—90.8% beträgt, zu einer auffallenden Abnahme der synthetisierenden Fähigkeit des Fermentes führt. Dabei wird die Hydrolyse bei der Sorte *Lutescens* 062 keinen wesentlichen Veränderungen unterworfen. Bei der Sorte «Markis» jedoch steigt gleichzeitig mit der Abnahme der synthetisierenden Wirkung der Invertase ihre hydrolytische Aktivität sehr stark. Somit ist die volle Wassersättigung, welche bei den oberirdischen Organen der Pflanze als Resultat eines beweglichen Gleich-

gewichtes zwischen Verdunstung und Wasserversorgung durch Wurzelsystem zu Stande kommt, nie gleich der vollen Wasserkapazität, und was besonders wesentlich ist, der normale Verlauf der Fermentreaktionen wird nur bei voller Wassersättigung gesichert.

Es ist beachtenswert, dass die überschüssige Feuchtigkeit bei einer Reihe höherer Pflanzen ebenfalls zur Deprimierung des Assimilationsvermögens führt. So hat, z. B., Brilliant ([8]) bei Efeu ein Maximum der Photosynthese nicht bei überschüssiger Wassersättigung der Blattgewebe sondern bei Wasserregime, welche ihrer natürlichen Wasserbilanz entspricht, beobachtet. Eine

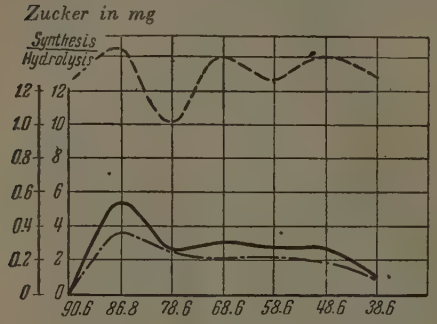


Abb. 1.

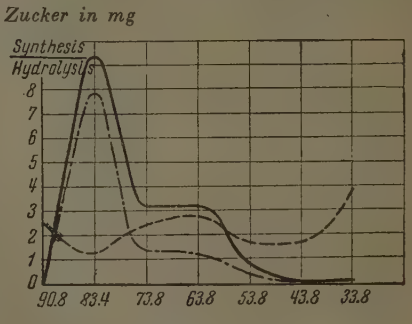


Abb. 2.

Abb. 1. Wirkungsrichtung der Invertase in den Weizenblättern *Lutescens* 062 in Abhängigkeit vom Wasserreichtum der Pflanzenzelle. Ununterbrochene Linie—Synthese, punktierte—Hydrolyse, gestrichelte — Verhältnis $\frac{\text{Synthese}}{\text{Hydrolyse}}$.

Abb. 2. Wirkungsrichtung der Invertase in den Weizenblättern «Markis» in Abhängigkeit vom Wasserreichtum der Pflanzenzelle. Ununterbrochene Linie—Synthese, punktierte—Hydrolyse, gestrichelte — Verhältnis $\frac{\text{Synthese}}{\text{Hydrolyse}}$.

merkbare Abschwächung der Photosynthese bei xeromorphen Pflanzen der Zuckerrübe bei überschüssiger Bodenfeuchtigkeit haben Kursanov, Blagoweschtensky und Kasakova ([9]) festgestellt. Die erwähnte Erscheinung bringen die Autoren mit der Verminderung der Anzahl der Interzellularräume und der Erhöhung des osmotischen Druckes in Zusammenhang, was nach ihrer Ansicht zu einer Abschwächung der Photosynthese führt. In den Versuchen von Aleksejev ([10]) hat die Erscheinung der Abhängigkeit der Assimilationsenergie vom Grade des Wasserreichtums der Pflanzengewebe eine weitere Bestätigung erhalten.

Somit unterdrückt die überschüssige Feuchtigkeit nicht nur die fermentative Tätigkeit der Pflanzenzelle, sondern übt auch auf die photosynthetische Aktivität einen wesentlichen Einfluss aus.

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den 13. IV. 1940.

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*GEOLOGY*

# NEW DATA FOR THE STUDY OF DEEP-SEATED VOLCANISM IN THE MINOR CAUCASUS

By V. N. KOTLIAR

*(Communicated by A. E. Fersman, Member of the Academy, 15. VII. 1940)*

The present paper contains the main conclusions made as a result of field observations in one of the most interesting regions of the Trans-Caucasia where a rare variety of intrusives of different composition and age are to be found. The region explored comprises an area of more than 1000 km² and is situated in the northern and in the central parts of Armenia.

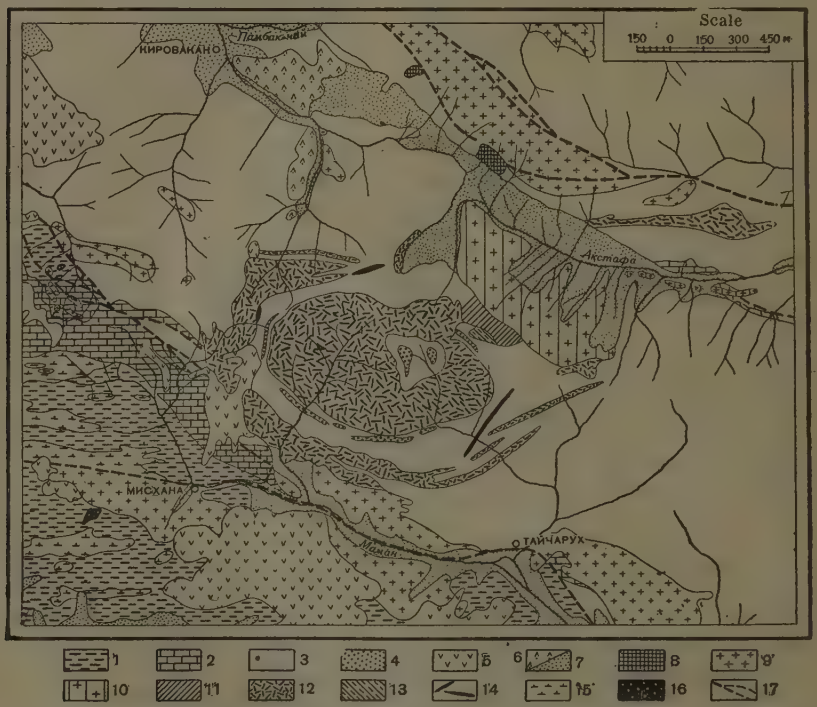
The principal morphological element of the region is the Pambak ridge, being itself the divide between the river systems of the rivers Kura and Arax. Also in latitudinal direction, north of it, passes the Halab and, south of it, the Miskhan ridge.

Geologically the region is composed of the ancient schist-rock bottom and volcanogenic rocks of Paleozoic or pre-Paleozoic age. Next we have an unconformably and transgressively occurrent bottom layer of the Cretacious period, consisting of series of conglomerates and sandstones of Cenoman stage, Turonian marl and limestones of the Senonian stage. Further the Senonian limestones are overlain by a volcanogenic stratum, up to 2.5 km thick, belonging to the Eocene. All the strata named are overlapped by an unconformably and transgressively occurring series of tuffbreccia and Oligocene lava. In the river valleys and along them Quaternary alluvium deposits, besides lava and tuffs, are widely distributed.

Tectonically this region represents the large Miskhano-Arzakend anticline passing north through a number of small crooks into the Pambak syncline which, in its turn, passes into the comparatively narrow Voskresenov anticline. This tectonic massif is dissected by numerous breaks for the most part of general Caucasian direction, some of which look as overthrusts. The largest break zones pass along the Fioletov-Voskresenov and the Maman depressions. A number of breaks cut across the whole region, even pass beyond its limits (that of Karanlug and the one of Sarykain). We encounter also traces of ancient pre-Cretaceous proper tectonics, but the age of the greatest number of breaks is Eocene proper. The most considerable interruptions in deposition of sediments together with wash-out of the rock masses took place before Cenoman and Oligocene.

The intrusive rocks are divided into two large groups: 1) ancient ones and 2) Paleogene. Among the ancient intrusions may be distinguished three massifs: 1) massif of intrusions of basic composition; 2) quartz-diorite and gabbro-diorite massif; 3) massif of leucocratic granite.

The first massif is represented by gabbro-gabbro-diabases, diabases and serpentines. The presence of ancient serpentine in the Minor Caucasus has been established for the first time by myself. One of the chief peculiarities of this massif is the considerable schistosity of the intrusions and their belonging by composition to the ancient schist-rockness. This is why I feel inclined to fix their age in accordance to the age of this part of the schist-rockness, i. e. pre-Paleozoic. The second massif is represented by one so-called Agviran massif that had formerly been taken for Tertiary. Still, the presence of pebbles of same rocks in the conglomerates of Cenoman, moreover its fault




*1.* Paleozoic—pre-Paleozoic—metamorphic schists. *2.* Upper Cretaceous—conglomerates, sandstones, marls and limestones. *3.* Eocene—volcanogene beds. *4.* Eocene,—alkaline effusives and their tuffs. *5.* Oligocene—lavas and tuffaceous breccias. *6.* Quaternary lavas. *7.* Recent alluvial deposits. *8.* Upper Eocene—gabbro. *9.* Upper Eocene—granodiorites, quartz tephrites, quartz monzonites etc. *10.* Upper Eocene—porphyry-like granites. *11.* Upper Eocene—syenites. *12.* Upper Eocene—nephelinic, alkaline and pseudo-leucitic syenites. *13.* Upper Eocene—nordmarkites and monzonites. *14.* Upper Eocene—dykes of epileucitic porphyries. *15.* Paleozoic granites. *16.* Pre-Paleozoic hyperbasites. *17.* Tectonic breaks.

produced by plagiogranite, mentioned by Paffenholtz (1), induced me in favour of ancient age, obviously Paleozoic. The prevailing representative of the third massif is plagiogranite, energetically and almost everywhere injecting into the schist-rockmass. Neither among Jurassic nor among Cretaceous intrusions in the Minor Caucasus are such rocks to be encountered. The pebble of plagiogranite has also been found in Cenoman conglomerates, presenting the very earliest formation following the ancient ones, i. e. the schist and the volcanogene rockmass. Thus, the age of this massif has to be

assumed as Paleozoic, possibly corresponding to one of the phases of post-Caledonian or Variscian folding.

The Paleogene or, to be more more exast, the Eocene cycle is represented by consecutive intrusions with formation of the following intrusives (to begin with the earlier ones up to the young ones): 1) pyroxenite and gabbro; 2) quartz-diorite, granodiorite and quartz-monzonite with rapidly following intrusives of granite and granodiorite; 3) porphyraceous granite (Pambak): 4) syenite; 5) alkaline, nephelite and pseudoleucitic syenite that were preceded by dykes of epileucitic syenite and, evidently, also by epileucitic porphyry and tephrite; 6) nordmarkite and monzonite.

The relative age of all the types of rock mentioned above—from the ancient ones to the young ones—may be determined rather reliably on ground of geological field evidence, except for the last type—monzonite which, in compliance with petrographic considerations, has been put down for the youngest.

All the intrusions listed above occurred within the Eocene proper. Oligocene lava, for the age of which Paffenholtz (2) has given us the proofs, overlaps the quartz-diorite and the alkaline intrusions and does not show any traces of the intrusions bearing upon it. The largest interval of time took place between the formation of the massifs of basic and granodiorito-monzonitic composition, on the one hand, and on the other, between the porphyraceous granite and the massif of alkaline intrusions. This conclusion has been adopted both on the grounds of their direct mutual relations and by reason of the sharply different behaviour of the intrusions of these two groups towards tectonic breaks.

The intrusions of pyroxenite and gabbro are sparsely distributed. Among them ball-gabbro of fine quality has been encountered; this is the second case of such rocks having been found in the USSR. It has been ascertained that the formation of pyroxenite and the variety of gabbro were not simultaneous but pulsating. At first the pyroxenite and large grained gabbro were formed, next the ball-gabbro and later on fine grained gabbro-norite. These rocks are obviously synchronous to the Gokcha intrusives of basic composition, but already adapted to another tectonic range passing further down south of the Gokcha overthrust, a fact which makes us take a different view concerning the distribution of these rocks in the Minor Caucasus. Gabbro is strictly confined locally together with intrusions of quartz-diorite and monzonite which are by far more widely distributed than the former. Taking this into consideration together with certain petrographic data, I consider these massifs genetically related to each other, while in the formation of the second massif the phenomena of hybridism seem to have played the main rôle. An essential rôle was obviously played by these phenomena in the formation of porphyraceous granite which has many properties in common with granite of the «Rapakivy» type. Porphyraceous granites contain a tremendous number of modified xenoliths.

Alkaline intrusions are, in the main, situated on the Pambak ridge between two large break zones—the Fioletov-Dilijan and the Miskhano-Maman zones—on a site among relatively little dislocated rocks of the Eocene volcanogene rock bottom. Besides this, they are surrounded, almost on all sides, by intrusions of quartz-diorite and quartz-monzonite. Taking all the alkaline intrusions as a whole, they cover an area of 63.8 km$^2$. Very typical is the concentric structure of alkaline intrusions with one central massif of ellipsoidal outlines which is surrounded with ring-like distributed, narrow intrusions that frequently pass into dykes.

The petrographic composition of the nephelite-syenite is characterized by its content of orthoclase, frequently microperthitic nepheline, plagioclase (No. 20—41), alkaline hornblende belonging to the hastingsitic order, aegi-

rite or aegirite-augite (these latter ones not always being present), biotite, analcite, fluorite and melanite. The presence of this last one is very characteristic, and so is the presence of pseudomorphoses after leucites, filled largely with zeolites, muscovite, at times with cancrinite and not often with scapolites. Of mineral admixtures there usually are: sphene, apatite, titanomagnetite and zirconium. We have to emphasize the leucocratic nature of the nepheline and alkaline syenites, which may be seen from the relatively small quantity of dark-coloured minerals, ordinarily not exceeding 10—15% of the rocks.

With the reduction of the quantity of nepheline the rocks gradually change into alkaline syenite. Among varieties of intrusions in alkaline rocks aegirite-nepheline and pseudoleucitic syenite have been noted. In the dykes epileucitic porphyry [according to Zavaritsky ([1])] and also jade have been found.

Large and beautifully shaped crystals of leucite already replaced (up to 12 cm in size) have been observed in epileucitic porphyry. These rocks, as mentioned by me before ([2]), are the first finding of such formations in the Caucasus.

Of particular interest is the association of the alkaline massif with monzonite. An important peculiarity of the Pambak alkaline massif is the close local and genetic relation between the intrusives and the alkaline effusives, in particular that with the epileucitic porphyry with its tuffs and tuffbreccia. The study of alkaline intrusives clearly shows that the intrusions were formed soon after ejections of alkaline lava; the doubtlessly common generic features of the magmatic material that originated the formation of the lava, the tuffs and the intrusives of this composition, point to this.

The metallogenesis of this region is characteristic for its small agency in mineralizing the ancient intrusions, ceasing only with the feebly displayed appearance of non-ferrous metals and alluvial gold and by a much more important rôle of the Paleogene intrusions. In this respect the most important is the upper Eocene massif of quartz-diorite, granodiorite and quartz-monzonite with which numerous deposits of non-ferrous metals and but few deposits of rare metals are related. The great rôle played by these intrusions in the Caucasian metallogenesis has not been known at all up to now. At the present time among the number of commercial deposits are that of sulphuric pyrite (Tanzut) and the one of alluvial gold (Golovinskoye). Now it is time to raise the question of investigating the radioactive zirconium found in the slicks near the village Voskresenovka. We also deem it expedient that the loose Quaternary formations on the western and the southern slopes of the Miskhan ridge be explored for diamonds.

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Leningrad.

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*MINERALOGY*

# SOME NEW DATA ON FLUORITE AND CELESTITE IN THE KUNGURIAN DEPOSITS OF THE URAL-EMBA REGION

By V. P. BATURIN

*(Communicated by W. I. Vernadsky, Member of the Academy, 9. VII. 1940)*

The investigations conducted during the past year gave some new interesting material as to the distribution of fluorite and celestite in the Kungurian deposits of the Ural-Emba region. Following the detection of fluorite in the cap-rock of the Zamiatin (1) salt dome this mineral was found in the normal bedded Kungurian deposits of the Aktiubinsk region. Here fluorite was encountered in the insoluble residue of a limestone from the Sholaksai anticline section.

As in the previously described carbonate rocks of the Zamiatin dome, the insoluble residue of the limestone from the Sholaksai river is largely represented by celestite. The celestite content of the rock is up to 40%, which makes it closely resemble the above celestite limestone of the Zamiatin dome. The fluorite makes up only a negligible part of the insoluble residue (much less than 1%); i. e. its quantity is much lesser than in the carbonate rocks of the Zamiatin dome. Fluorite inclusions in celestite grains are frequently observed. The fluorite is crystallized in cubes, but more frequently in irregular grains; the size of these (as well as that of the crystals) does not exceed some hundredths of a millimeter.

While in the previously described carbonate rocks of the Zamiatin dome a more or less uniform penetration of celestite into the carbonaceous groundmass has been observed, in the present case a study of thin-sections showed that celestite fills up cavities and fissures, being without doubt a secondary formation. Inasmuch as fluorite is present in the shape of inclusions in celestite, its origin in the Sholaksai limestone is secondary, too.

These observations make us critically revise our previous conclusion as to a simultaneous precipitation of carbonates and F and Sr compounds from solutions. Although the above-described phenomenon of secondary transference of Sr has not been observed in the carbonate rocks of the Zamiatin dome, their celestite content, however, is of the same order as in the limestone of Sholaksai. It is very probable that in the cap-rock of the Zamiatin dome a secondary transference of fluorine and strontium takes place resulting in a high concentration of these in the carbonates.

The data obtained on the forms of segregation of celestite and fluorite do, of course, not exclude the precipitation of $SrSO_4$ and $CaF_2$ in carbonate rocks. With regard to fluorite this process has been studied in detail by Pustovalov (2) who came to a conclusion that in Carboniferous dolomites $C_2$

«fluorite crystals are to be regarded as syngenetic formations». According to Pustovalov, fluorides are carried away herefrom and accumulate in considerable quantities in marls.

Mineralogical studies of Kungurian rock salt, conducted by us along with analyses of the insoluble residue of the carbonate rocks of the Ural-Emba region, indicate also other sources of primary fluorite.

Before we pass to a description of the results of these investigations, a few words are to be said on the methods of isolating the insoluble residue from chlorides, which made it possible to detect the accessory minerals contained in these in negligible quantities. After having solved 200—500 g of rock salt in distilled water, the insoluble residue obtained was freed from argillaceous particles by decantation, dried and separated by means of Thoulet's solution in a Moshev centrifugal apparatus.

As the predominant element of the insoluble residue of rock salt is always anhydride constituting often 99.99% of the former, Thoulet's solution with a specific gravity 3.0 was used. The specific gravity of the anhydride being 2.9, it gets entirely into the light fraction, while a number of heavier minerals concentrated within the heavy residue.

While analyzing the heavy fractions of insoluble residues of rock salt from the Dossor, Shubarkuduk and Aschebulak salt domes, fluorite has been detected in a number of fractions, accompanied with considerable quantities of celestite as in carbonate rocks. Fluorite is also contained here in lesser quantities as compared to celestite; but while in the heavy fraction of limestones fluorite is encountered as single grains among celestite, in rock salt the quantity of the latter mineral is only several times greater than that of the former, and in some cases the quantity of fluorite closely approaches that of celestite.

The fluorite from rock salt forms exceptionally well developed cubes (frequently flattened down to tetragonal tablets). The crystals are much larger than in the limestones studied. Sometimes their size is up to 0.2 mm.

While celestite is present in all investigated samples, being a constant accessory mineral of rock salt, fluorite is characteristical only of certain horizons. This is quite normal, if it be remembered that the Sr-content in sea water is considerably higher than the F-content.

The fluorite and celestite of rock salt are undoubtedly primary formations precipitated from a solution simultaneously with NaCl. As rock salt beds were dissolving, fluorine and strontium were carried away by waters and fixed in carbonate rocks in the form of calcium fluoride and sulphate of strontium. If the solution brought about a complete lixiviation of the salt layer, its existence could be easily overlooked later on in the section, especially if the thickness of the layer had not been very considerable. In salt domes the upper portion of the stock often becomes truncated under the influence of underground waters; this is a phenomenon frequently observed, leading to the formation of a flat surface of the salt dome, to which American investigators gave the name of «salt table». It is evident that this process must bring into solution considerable amounts of strontium and fluorine which are isolated as celestite and fluorite in the rocks overlying salt, the caprocks.

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*MINERALOGY*

# ON THE COMPOSITION OF JAROSITES FROM THE DEPOSITS OF CENTRAL KAZAKHSTAN

By F. V. CHUKHROV, R. E. AREST-YAKUBOVITCH and N. A. KOZLOVA

*(Communicated by A. E. Fersman, Member of the Academy, 22. IV. 1940)*

Jarosites belong to the most typical hypergene minerals of the ore-deposits of Central Kazakhstan. Their formation is usually connected with the weathering of pyrite, but it may also occur at the expense of marcasite and pyrrhotite. Jarosites are encountered most frequently in those deposits which are characterized by the absence of any considerable segregations of lead, arsenic and partly copper minerals in the composition of sulphite ores. In the presence of lead, arsenic and copper complex ferruginous sulphates, sulphate-phosphates and sulphate-arseniates may be formed (beaverite, corkite and beudantite).

The present Note contains data on the chemical composition of jarosites from different deposits of Central Kazakhstan. The analyses have been made by R. E. Arest-Yakubovitch (analyses 1, 2, 3, 5, 6, 7) and N. A. Kozlova (analyses 4, 8, 9, 10). The deposits from which originate the jarosites studied by the present authors are located in the following regions: in the Karaganda region—the deposits Shoptykul, Berkara, Kounrad and vein No. 43 of the Shaitantass group; in the Pavlodar region—the Maikain and Alexandrovskoye deposits; in the Akmolinsk region—the Stalinskoye deposit.

Table 1

| Constituents | Sample Nos. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| $Na_2O$ | 5.16 | 5.47 | 5.44 | 5.69 |
| $K_2O$ | 1.10 | 0.62 | 1.19 | 0.43 |
| BaO | — | — | 0.75 | — |
| CaO | 0.15 | 0.09 | 0.16 | 0.60 |
| MgO | 0.00 | 0.00 | 0.00 | 0.05 |
| PbO | 0.06 | traces | traces | — |
| CuO | 0.00 | 0.00 | 0.00 | — |
| $Fe_2O_3$ | 49.20 | 49.01 | 47.75 | 47.84 |
| $Al_2O_3$ | 0.03 | 0.33 | 0.02 | 1.44 |
| $Mn_2O_3$ | traces | traces | traces | 0.05 |
| $SO_3$ | 32.55 | 32.77 | 31.90 | 32.10 |
| $P_2O_5$ | 0.27 | 0.31 | 0.44 | 0.22 |
| $As_2O_5$ | 0.04 | 0.08 | 0.00 | — |
| $TiO_2$ | 0.18 | 0.08 | 0.05 | 0.00 |
| $SiO_2$ | 0.46 | 0.54 | 2.03 | — |
| $H_2O^+$ | 10.40 | 11.28 | 11.48 | 10.94 |
| $H_2O^-$ | 0.05 | 0.05 | 0.10 | 0.00 |
| Insoluble residue | — | — | — | 0.05 |
| Total | 99.65 | 100.63 | 100.31 | 99.41 |

Jarosites are most abundant in the Maikain deposit especially in section «C». Accumulations of the purest jarosite are represented here largely by concretional aggregates up to 1 m in diameter. The data of analyses of the Maikain jarosites are given in Table 1. As may be seen from these data the jarosites analyzed may be called sodium-jarosites.

1) 50 m horizon, shaft No. 2, eastern drift. Schistose finely-scaled jarosite of a brownish-yellow colour.

2) 50 m horizon, shaft No. 2, horizontal drift No. 1. Finely-crystalline jarosite from the outer portions of the jarosite concretion. Shows traces of a concentric laminated structure. Yellow colour.

3) 50 m horizon, shaft No. 2, horizontal drift No. 1. Finely-crystalline brownish-yellow jarosite forming segregations among the barite.

4) 40 m horizon, shaft No. 5, horizontal drift No. 1 bis. Brownish-yellow compact finely-crystalline jarosite from the inner portions of the jarosite concretion.

An idea as to the composition of jarosites from other deposites of Kazakhstan is given by Table 2.

Table 2

| Constituents | Sample Nos. | | | | | |
|---|---|---|---|---|---|---|
| | 5 | 6 | 7 | 8 | 9 | 10 |
| $Na_2O$ | 4.70 | 3.08 | 0,36 | 2.81 | 4.88 | 4.98 |
| $K_2O$ | 0.35 | 5.29 | 7.31 | 4.58 | 0.64 | 1.28 |
| CaO | 0.29 | 0.20 | 0.20 | 0.51 | 1.20 | — |
| MgO | 0.00 | 0.00 | 0.00 | 0.00 | 0.09 | — |
| PbO | 0.47 | 3.66 | — | — | — | — |
| CuO | 0.25 | 0.09 | 0.00 | — | — | — |
| $Fe_2O_3$ | 54.55 | 45.00 | 45.57 | 47.20 | 52.36 | 48.72 |
| $Al_2O_3$ | 0.35 | 0.20 | 0.28 | 2.40 | 0.67 | 0.36 |
| $Mn_2O_3$ | 0.52 | traces | traces | 0.06 | traces | 0.06 |
| $SO_3$ | 26.78 | 28.80 | 29.56 | 31.19 | 28.08 | 31.91 |
| $P_2O_5$ | 0.19 | 0.20 | 0.32 | 0.45 | 0.59 | 0.42 |
| $As_2O_5$ | — | 2.01 | — | — | — | — |
| $TiO_2$ | 0.00 | 0.04 | 0.04 | 0.00 | — | — |
| $SiO_2$ | 0.59 | 1.93 | — | — | — | — |
| $H_2O^+$ | 11.19 | 8.92 | 11.24 | 11.23 | 9.95 | 10.66 |
| $H_2O^-$ | 0.20 | 0.08 | 0.15 | 0.00 | 0.32 | 0.11 |
| Insoluble residue | — | — | 4.61 | 0.25 | 0.77 | 0.98 |
| Total | 100.43 | 99.50 | 99.64 | 100.68 | 99.55 | 99.48 |

5) Deposit Shoptykul. North-eastern section. Finely-crystalline yellow jarosite forming compact aggregates.

6) Deposit Berkara. Compact cryptocrystalline brownish-yellow jarosite, when hit falling to angular pieces.

7) Deposit Kounrad. Yellow finely-crystalline jarosite of a friable and compact constitution.

8) Deposit Alexandrovskoye. Compact finely-crystalline light-yellow jarosite.

9) Deposit Stalinskoye, Digger's area, pipe near shaft No. 1. Friable finely-crystalline brownish-yellow jarosite.

10) Neighbourhood of Mt. Shaitantas in the Dzeskazgan-Ulutav mining region, vein No. 43. Yellow jarosite of finely or cryptocrystalline constitution. Compact aggregates.

The above data show that among the jarosites studied by the authors sodium varieties are predominant. In connexion herewith it is worthy to note that, according to the data published, sodium jarosites in the deposits of the USSR are in general more widely spread than potassium jarosites.

The invariable presence of phosphorus (0.19—0.59% $P_2O_5$), aluminium (0.02—2.40% $Al_2O_3$), calcium (0.09—1.20% CaO) is characteristic of the jarosites under description. The manganese content varies from traces to 0.52% $Mn_2O_3$. Magnesium is either absent, or contained in hundredth of a per cent. In jarosites from Shoptykul lead is combined with phosphorus, while in jarosites from Berkara it is combined with arsenic. Barium detected in one of the samples of Maikain jarosite (analysis No. 3) is combined in the form of barite. The admixture of copper is most considerable in jarosite from Shoptykul (0.25% CuO). Titanium belongs to the non-characteristic admixtures to jarosites (0—0.18% $TiO_2$).

Selenium forms an admixture characteristic of the Maikain jarosites. This element has been found also in jarosites from the following deposits: Shoptykul, Stalinskoye and Alexandrovskoye. A part of the Maikain jarosites is enriched in gold and silver. Gold in Maikain jarosites is represented by native segregations, and silver—by mineral halides, chiefly embolites.

Aside from quantitatively determined elements, the following elements have been found spectroscopically in individual samples of jarosite: vanadium, gallium, indium, molybdenum, tin, silver. Lines of bismuth have not been detected or only traces of it have been observed.

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*GENETICS*

# IN RESPONSE TO AN ARTICLE BY A. N. KOLMOGOROFF

By T. D. LYSSENKO, Member of the Academy

The Comptes Rendus of the Academy of Sciences of the USSR, vol. XXVII, No. 1, 1940, carries an article by the well-known mathematician A. N. Kolmogoroff, entitled «On a New Confirmation of Mendel's Laws». In his desire to prove the truth and invulnerability of Mendel's law, the author produces mathematic arguments, formulae and even curves. I do not believe I am competent to pass an opinion on these mathematical proofs and arguments. Moreover, as a biologist I am not interested in the question whether or not Mendel was a good mathematician. As to my opinion of Mendel's statistics, I have expressed it on many occasions in the press and I claim that they have no bearing whatever on biology.

What I wish to say in my short Note here is that Kolmogoroff's article, too, has no bearing whatever on biological science.

While explaining Mendel's principle of 3 : 1 segregation, Kolmogoroff says in his article that it makes no difference whether a single family or a group of many families, produced by different pairs of heterozygous parents of the *Aa* type, are taken for analysis.

Indeed, it may seem to Kolmogoroff that all the plants produced by different pairs of heterozygous parents of the *Aa* type are alike. But we, biologists, know that no two plants can be quite identical in their hereditary qualities. We know that in a family of the second generation of crossbred wheat, 150 out of 200 plants may be of the beardless type and 50 of the bearded one, but in another family of the same combination there may be as many as 190 beardless plants and only 10 bearded, and in a third family we may even find that all the 200 plants are of the beardless type, and so on and so forth. In other words, each family has its variety.

To Kolmogoroff this is of no interest, since his only concern is that the mean should coincide with the mathematical conclusions. But we, who are concerned with genetics and breeding work, cannot be indifferent to such phenomena.

If, for instance, we have singled out some wheat plants for reproduction within a family including a large ratio of the bearded type (50 out of 200), i. e. a family showing great variety, we may be sure that the progeny of selected plants will show great variety, too. Under such conditions selective breeding may prove hard and futile. It will be different, however, if we take seed from a family in which all of the 200 specimens are more uniform. For this reason seeds from various plants of the first generation of crossbreeds should not be mixed, but should be sown separately, each family apart.

That is why we, biologists, do not take the slightest interest in mathematical calculations which confirm the useless statistical formulae of the Mendelists.

Kolmogoroff's article is based on the results of Ermolaeva's work. But Ermolaeva in her work has shown that the progeny of various families of crossbred peas of the same combination vary, each in a different way, whereas according to Kolmogoroff the variety manifested by the plants of different families falls within the limits of the mathematically admissible error. We biologists, however, do not want to submit to blind chance, even though this chance is mathematically admissible. We maintain that biological regularities do not resemble mathematical laws. We are of the opinion that in this controversy between Kolmogoroff, Member of the Academy, and postgraduate Ermolaeva, it is Ermolaeva who is in the right, and not Kolmogoroff.

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*GENETICS*

# IS IT POSSIBLE TO PROVE OR DISPROVE MENDELISM BY MATHEMATICAL AND STATISTICAL METHODS?

By E. KOLMAN

*(Communicated by T. D. Lyssenko, Member of the Academy, 2. VII. 1940)*

In his article «On a New Confirmation of Mendel's Laws» (1) published in the Comptes Rendus of the Academy of Sciences, A. N. Kolmogoroff suggests a formula for the probability of deviation of the actual ratio between the number of individuals with a dominant and with a recessive factor from what is theoretically expected in accordance with Mendel's 3 : 1 principle. This formula offers a finer means of analyzing statistical data than the accepted one (by quadratic deviation), but is to be applied, as pointed out by Kolmogoroff, only to families with not too small a number of individuals. Kolmogoroff applies it to Ermolaeva's material (2) and shows that, despite the opinion of Ermolaeva herself, her material does not diverge from but fully agrees with the ratio 3 : 1.

Certainly, this work of Kolmogoroff, one of the most prominent mathematicians within and outside this country, who has developed a most perfect axiomatization of the theory of chances, is not to be objected if viewed from a purely mathematical angle, and his method of verifying the indicated statistical data is much superior to the simple method of verification by quadratic deviation. Though it may be noted at once that both curves given by Kolmogoroff for Ermolaeva's two series (Figs. 1 and 2) show a constant deviation of the empirical curve from the theoretical one, viz., almost throughout the interval $x$ we observe that the empirical $y$ is$\geqslant$ the theoretical $y$.

Unfortunately, however, instead of confining himself to the purely mathematical aspect of the matter, Kolmogoroff draws conclusions which go beyond the limits of mathematics, and declares himself in favour of Mendel and Morgan's genetics, claiming that Ermolaeva's material «has proved to be a new brilliant confirmation of Mendel's laws».

We can quite admit that Ermolaeva's work may contain crude errors in the application of the statistical method, but nevertheless we must brush aside this minor question and follow Kolmogoroff in the field of methodological problems. This is all the more necessary, since the adherents of Mendel and Morgan will see in Kolmogoroff's article «a mathematical proof of Mendelism». This error will be of doubtful service to them, for it will hinder them from adopting the conclusions arrived at at the conference convened by the editorial board of the magazine «Under the Banner of Marxism», in October 1939, on problems of genetics and breeding. These conclusions were summarized by M. B. Mitin (3) in his concluding address at that conference.

And in so far as these theoretical problems are intimately connected with problems of plant and animal breeding applied on an industrial scale, per-

sistence in one's fallacy is anything but harmless here. This applies in the first place to persons like A. S. Serebrovsky whose attitude was subject to violent attack in the course of the conference. Nevertheless, instead of blotting out his own errors of which he more than once feigned to repent, Serebrovsky gave himself up to mobilization of forces against the ideas of Darwin and Michurin. And probably it is with this aim in view that he called Kolmogoroff's attention to the article of Ermolaeva, as stated by Kolmogoroff himself.

Kolmogoroff's wrong conclusions, evidently, spring from his methodology, in the question as to the rôle of the theory of chances and statistics in the study of the processes of the material world. Dealing with this methodology Kolmogoroff writes ([4]): «... we therefore limit ourselves to a mere reference to the empirical origin of the axioms of the theory of chances and deliberately set aside the profound philosophical researches on the concept of chance in the world of experiment». In his analysis of the pre-requisites for the application of the theory of chances to the world of realities, he has to a large extent followed Mises' conclusions (cf. R. v. Mises, «Wahrscheinlichkeitsrechnung», 1931, SS. 21—27, section «Das Verhältnis der Theorie zur Erfahrungswelt»).

In a more recent work of his, viz., «Analytical Methods in the Theory of Chances» ([5]) published in 1938, Kolmogoroff makes no changes or corrections in this most important point. We shall therefore turn to the indicated work by Mises. Indeed, on p. 22 of the said work we find a clear-cut formulation of the relation, in which the theory of chances stands to reality according to Mises: «The theory based on the two axioms—existence of limits and their insensibility to the choice of place—may claim that it is a mathematical theory, that like the theoretical construction of geometry it can only be verified by the laws of reasoning...»

Even those who have but a slight knowledge of philosophy will see what the epistemological roots of this proposition really are. But to leave no room for doubt, Mises refers the reader to another work of his ([6]) which, as he says, reveals the philosophical bases of his principles. In this work, on p. 182, we read that in questions pertaining to language, conception and substance, he, Mises, «mainly upholds the point of view of Mach». On p. 152 Mises relates that the physicists' views of the atom as a really existing substance «had to be replaced by the more general view anticipated by Ernst Mach, who holds that neither space nor time in the ordinary sense of the word can be applied to the atom». This idea is further developed on p. 153: «In our time of rapidly changing periods of physics, the «mechanistic» period with its prevailing belief in the absolute reality of the atoms was but too short-lived». And then on p. 178: «With an obstinacy, easy to explain psychologically, people to this day cling to the deeply rooted old habits of reasoning associated with the so-called law of causation».

These quotations are more than sufficient to show that Mises is a true follower of Mach, and his views on the relation of theory to reality are the same as those which were subjected to destructive criticism by Lenin in his «Materialism and Empiriocriticism». To follow the views of Mises to any extent (let alone to a large extent) is in no way to be recommended.

It is quite clear that he who, along with Mises, believes that the theory of chances is a theory that can be verified only by laws of reasoning and that in relation to reality (called by Machists the world of «experience») scientific theories play only a descriptive rôle, is incapable of properly formulating, let alone solving, the question of the limits of the applicability of the theory of chances, or the limits of the perceptional significance of this theory for some science, say biology. Many genetists, Johansen for instance, recur to

such Machist views on the relation of theory to reality not merely for fixing the rôle of statistics, but are also making wide use of them throughout their genetic theories, beginning with the gene which is declared to be «a convenient conception», a «working hypothesis», and so on.

However, from the fact that Ermolaeva's or anybody else's data happen to be in agreement with Mendel's «law» of 3 : 1, it only follows, as noted by us (7) in connexion with Enin's (8) work, that these data are compatible with Mendel's probability scheme, but by no means does it follow that they prove or confirm Mendel's biological conception. It is precisely in this light that the question is regarded by S. N. Bernstein who writes (9) that the results of crossing peas show compatibility with Mendel's hypothesis. Now while incompatibility of some material with a given theory disproves the latter, compatibility neither proves nor confirms this theory, for the same material may prove to be compatible also with other theories.

In concrete science, such as political economy, physics, biology, the theory of chances and the statistical method of investigation are merely auxiliary instruments. It depends on the concrete theory controlling the statistical method whether or not this method will yield results that truly reflect reality. It is now generally known that statistics based on a false economic theory when applied to social phenomena gives unscientific results. It is also known that in physics the application of a certain statistical method—Fermi-Dirac or Bose-Einstein—is dictated by physical conditions and not by statistical considerations as such. The same applies to biology if only it is treated as a science. Variational statistics may and should be applied to it but only on condition that it is controlled by biological theories and by no means should it be intended to replace these theories.

It was this that we tried to explain in our short Note on T. K. Enin's material, but Kolmogoroff ignored this main point and only rebuked us for not having applied to Enin's data his, Kolmogoroff's, fine analysis, although with reference to these data he himself said: «His material, however, is far from being abundant (25 families against the two series of 98 and 123 families in Ermolaeva's paper), and some other doubts are apt to arise about it. The author himself considers his data as not entirely uniform. We shall not enter, therefore, into detailed analysis of them». Moreover, the only conclusion made by Kolmogoroff in connexion with Enin's material is as follows: «An indication of such an excessive approximation of the frequencies of $\frac{m}{n}$ to $\frac{3}{4}$ is contained in the data secured by Enin». But we have arrived at the same conclusion, though, perhaps, by more crude means which, however, for Enin's data were good enough. We have pointed in our Note in the «Vernalization» to «the perfect, perhaps too perfect, coincidence between the empirical and the theoretically calculated frequencies».

Equally surprising is the fact that Kolmogoroff overlooked another point in our criticism of Enin's paper—arbitrary classification of characters. This is an important point, for the basis of classification (which stalks are to be considered long and which short, which as having and which as having not yet taken on colour) will affect the results in a most sensitive manner.

From all this, as well as from the way Kolmogoroff formulates the biological aspect of his problem, it is clear that, irrespective of his fine method of verifying statistical data which he recommends instead of the cruder method, he was guided in his article by a preconceived biological idea. Of course, owing to the extreme simplicity of the admissions on which it is based, Mendel-Morgan genetics, representing an apparently practical domain, leaves nothing to be desired as a field for mathematical exercises. And indeed, ma-

thematicians, including A. N. Kolmogoroff, have, from the mathematical point of view, produced extremely interesting works, based on schemes of formal genetics. Why genetics is so attractive for mathematicians is best of all revealed by D. Hilbert, the most prominent of contemporary mathematicians. He writes ([10]): «The *Drosophila* is a little fly, but we take a great interest in it. It has been used extensively in breeding experiments. Usually of grey colour, with red eyes, without spots, with round and long wings, it sometimes shows certain deviations: yellow specimens are found with white eyes instead of red ones, and so on. Ordinarily, five characters go together. For example, if the fly is of a yellow colour, it will be plumose and will have white eyes and split and cloddy wings. When crossbred, however, the progeny shows comparatively sharp deviations from these combinations of characters. These deviations occur in a definite proportion. The figures, thereby obtained experimentally, correspond to Euclid's linear axioms of congruence as well as to the axioms related to the geometrical concept of «between». Thus, the laws of heredity appear as an application of the linear axiom of congruence of the elementary geometrical propositions about plotting the intercepts; it is so simple and precise and at the same time so wonderful that it would hardly be surpassed by the boldest imagination».

Having utterly simplified the biological conception of the wonderful bases of heredity and having reduced them to a combination of genes linearly arranged or to a scheme of urns with little balls that remain immutable and inaffected by each other, they find that geometrical axioms may be applied to these conceptions and are elated over it. What matters it if this biological «simplicity» is tantamount to meaninglessness so long as it gives them universal laws!

A. N. Kolmogoroff is wrong when he says that the upholders of the Mendel-Morgan genetics do not insist on the general, universal nature of Mendel's laws. On the contrary, what is typical of our contemporary Mendel-Morganists is that they have turned Mendel's good rule of the mixing of factors, deduced from the results of cross-pollination of peas and explained by him by the theory of chances, into a universal law, into a general theory of heredity. Thus, a statistical rule (and a particular one at that) which can only give a quantitative picture of the outward effects of processes, is turned into a biological law (a universal one to boot) which allegedly controls the inner causes of these processes and hence explains them. Here is K. A. Timiriazeff's opinion of this «law» ([11]): «According to the followers of Mendel, this law has the same significance for biology as the law of gravitation for astronomy or Dalton's law for chemistry... Undoubtedly, Mendel has an advantage over his fanatical followers—it is his sober, balanced attitude to the obtained results, which he never considered to be a universal law...».

In summing up, we wish to emphasize once more that if Mendel's law is a biological law, it cannot be proved or disproved by mathematical or statistical means. Only on the basis of biology, by making use of the vast cytological, histological, biochemical material, the material on the mechanics of development and so on, can Mendel's law be proved or disproved as a universal biological law. In doing this one must go over the available material with a critical eye, and if the hard facts demand it, one should not be afraid of attacking the very foundations of genetics. Mendel's law of segregating factors deduced from a definite group of cases of inheritance is nothing but a statistical rule, and not a universal biological law. It is, moreover, a rule which essentially depends on the mode of classifying factors. Finally, it should not be forgotten that statistics as applied to biology must occupy a subordinate place. According to Engels ([12]) and Lenin ([13]), the higher the form of movement, the more difficult it is to apply to it the mathematical

method and the less effective is this method for the perception of reality.

For these reasons it is obviously futile to prove or disprove Mendel's law by statistical and mathematical methods.

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*GENETICS*

# PHYSIOLOGICAL DISCONTINUANCE OF ONTOGENESIS AND THE PRODUCTION OF DIRECTED MODIFICATIONS

By M. E. LOBASHOV

*(Communicated by I. I. Schmalhausen, Member of the Academy, 4. IV. 1940)*

The problem of obtaining directed or definite modifications is especially interesting and important in connexion with the parallelism existing in the external manifestation of hereditary and non-hereditary changes ([1], [2]). Although this problem is no longer new, very little is known about the general regularities underlying or controlling the process of developmental variation.

One of the main conditions for the mass production of unitypical (and directed) modifications should be their discontinuous emergence. At the same time, beginning with the mutation theory of De-Vries the current point of view considers that modifications differ from mutations by an uninterrupted series of changes. The point of view as regards the uninterrupted arising of non-hereditary changes must, evidently, be altered and the latter must be considered just as discontinuous as the hereditary changes. In this case it is only necessary to admit the physiological or biological discontinuance of ontogenesis.

Modifications, as well as mutations, emerge intermittently and their continuity is called forth by the character of their subsequent development. The continuity of modifications is explained, on the one hand, either by the asynchronity in the process of a particular reaction taking place in different individuals of the population, or by the development of unitypical organs and characters of one organism, and on the other hand, by the extension of their development in time and by the action of different combinations of environmental factors in various phases of their development.

On the basis of the available experimental findings the physiological and biological discontinuance of the development of the organism is considered to be a widespread phenomenon. In the process of its development the character has a beginning and various critical and sensitive periods. T. D. Lyssenko has given one of the most obvious proofs of the existence of physiological discontinuance by establishing the physiological developmental phases in plants.

Recent investigations on the experimental production of phenocopies ([1]) and roentgenomorphoses ([2]) have furnished unmistakable evidence of the physiological discontinuance of ontogenesis. The presence of «sensitive periods» for the production of definite types of phenocopies indicates the «step-like» physiological development of the organism.

It was shown ([3], [4], [5]) that the development of a character goes through a «sensitive period» which falls within the time, when usually the morpho-

genetic determination of the organ is taking place. The changes brought about in the character by an effect produced during the sensitive period may become apparent much later, after the formation of the organ (for instance, the formation of wing notches in *Drosophila* through the cytolysis of the formed wing). The investigations of this kind were carried out on pronounced phenotypical changes, but the possibility is not excluded that the development of any morphological character goes through the sensitive period. The presence of such periods indicates that the physiological development of a character or organ is not a uniformly proceeding process.

Experimental-embryological investigations confirm this lack of uniformity in physiological development. Numerous findings in this domain show, first, the presence of a certain sequence in the processes of growth and differentiation and the unequal rate of their course at various stages of embryogenesis; secondly, they indicate the presence of critical periods in embryogenesis, preceding or falling directly within the most intense period of differentiation.

Physiological discontinuance is a general law in ontogeny. I believe it to lie at the foundation of the discontinued emergence of phenocopies or modifications, which makes it possible to obtain directed modifications by means of the effect of external factors on a certain sensitive period.

The well-known experiments of Lyssenko on the transformation of hereditary winter forms of wheat into non-hereditary summer wheat forms are an obvious illustration of the above. Goldschmidt (6), summarizing the available data on the experimental production of phenocopies, concludes that formulae may be constructed for calling forth definite or desired phenotypes of *Drosophila*. Some phenotypes may be called forth during a very short period, others may be stimulated during a longer period of development, while others again may be produced under the action of specific environmental factors.

However, the production of unitypical and directed modifications in mass, especially characters with short sensitive periods, may be interfered with seriously by the fact that all treated individuals will not go through their sensitive periods simultaneously. The asynchronous course of a short sensitive period in the group of treated individuals is probably the main obstacle in the way towards the production of unitypical phenocopies or modifications.

The present preliminary report is devoted to the elucidation of this problem.

Two lines of *Drosophila* «Samara» and «Bukhara», bred for three years under laboratory conditions, served as test-material for the present investigation. No unitypical developmental variation was observed in the bulk of these flies during the above space of time.

In order to produce a most homogeneous material as regards age, short-term egg-deposits were obtained (6—8 hours). However, this method does not guarantee material of the same age, since after such egg-lying the developmental period is greatly prolonged. A safer method had to be applied in order to obtain a synchronous course of one of the sensitive periods. Since the peculiarities of the sensitive period play no rôle here, only its synchronous run during the action being important, any kind of external, well expressed physiological index, which might serve for the selection of the individuals, had to be chosen. The moment of the emergence of larvae from the nutritive medium before pupation was chosen as index. The larvae emerging from the nutritive medium on the walls of the bottle, were gathered during two hours 14—16 hours before X-raying. In this way material of the same age was obtained.

Pupae of an early age were X-rayed (4000 and 3000 r). Before and after irradiation the cultures were kept at 24—27° C. The flies emerging from

the treated pupae, were examined for phenocopies. Two experiments were carried out.

In the first experiment the pupae (the line «Samara») were X-rayed with 4000 r. This dosage proved to be too high, and a great mortality ensued. All the flies without exception had changed, and externally (position of the wings) they did not differ from the known dominant mutation *Dichaete*. The second experiment was carried out with a dosage of 3000 r applied to two different lines («Samara» and «Bukhara»). The method of selection was the same. The results of these two experiments are shown in the table.

Frequency of Occurrence of Phenocopies *(Dichaete)* under the Effect of X-rays in Pupae of *D. melanogaster*

| Nos. of exp. | Line | Dosage applied | ♀♀ | | ♂♂ | | ♀♀ and ♂♂ | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Total of flies examined | Number of flies with character | Total of flies examined | Number of flies with character | Total of flies examined | Number of flies with character | % of flies with character |
| 1 | «Samara» . . . . . | 4000 | 39 | 39 | 4 | 4 | 43 | 43 | 100.0 |
| 2 | » . . . . . | 3000 | 164 | 162 | 67 | 67 | 231 | 229 | 99.1 |
| | » . . . . . | 3000 | 117 | 110 | 23 | 23 | 140 | 133 | 95.0 |
| | «Bukhara» . . . . . | 3000 | 111 | 71 | 88 | 72 | 199 | 143 | 71.8 |
| | Total . . . . | — | 431 | 382 | 182 | 166 | 613 | 548 | 89.4 |

The table shows that in the first experiment 100% of unitypical changes (of the type of divergent wings) were obtained. In the second experiment the per cent of unitypical phenocopies fluctuates from 95.0 to 99.1% in the «Samara» line. The frequency of occurrence of phenocopies in the «Bukhara» line is much lower than that in the «Samara» line. The following fact is noteworthy which took place in the experiment with the «Bukhara» line. At the beginning of the emergence all the flies had changed wings and at the end of the summer (3—4 days after the start) flies with normal wings were found. The decreased frequency of occurrence of phenocopies in the «Bukhara» line (when the pupae were treated) and the emergence of flies with changed wings at the beginning of the flight, shows that one and the same sensitive period is connected in a different way with the pupation of the two races. Thus, an instance of a more feeble correlation between a separate sensitive period and the general development of the organism (here with pupation) in the «Bukhara» line is shown. Therefore, the differences in the genotypes (races) as regards the formation of separate phenocopies, observed by Goldschmidt, may be explained by a shift of the sensitive periods in the development, and not merely by their genotypic specificity to produce different phenocopies.

Thus, the total for the experiments shows that among the general number (613) of flies examined, 548, or 89.4%, proved to be unitypically changed. The changes were so well expressed that no difficulties were come across in their classification. A detailed examination of the phenocopy obtained showed that all the flies bearing the character divergent wings, had at the same time vertically upraised scutellar bristles. This indicates the presence of a close interdependence between these two characters, which is usually observed as a pleiotropic effect in wing mutants.

The examination of the experimental flies for the phenocopy of the notch wing type showed, that the frequency of its occurrence does not exceed the

per cent of spontaneous notches arising without any treatment. It is known that the sensitive period for the formation of notches on the wing is referred to the larval stage. The notch is formed (by means of degeneration) after the wing has formed, i. e. much later than the X-raying of the pupae has taken place. Therefore, the action of the X-rays, applied after the sensitive period had passed, proved inactive.

The mass occurrence of unitypical changes, undistinguishable from known mutations (in *Drosophila*), cannot be left without verification. Therefore, a total of 60 pairs of flies bearing this character were taken in order to be checked for inheritance. In the following two generations several thousands of flies were examined, and only single flies marked by the character of the parents were found. These single flies were also checked, and the character did not prove inheritable. Thus, the changes obtained in the experiments were typical phenocopies.

The mass occurrence of unitypical changes in our experiments we explain exclusively by the fact that the X-rayed material was of the same age. This confirms the above considerations as regards the importance of the synchronous run of the sensitive period during a shock action, in causing unitypical modifications. The data available in the literature, as well as our small experiments, make the general conclusion possible that modifications may be as definite as the phenotypical changes caused by recombinations of hereditary factors. The plasticity of ontogenesis as regards the capacity to produce variations is apparently exceptionally high. Nevertheless, it is at the same time natural to assume, that the amplitude of developmental variation highly exceeds the variation possibilities of the genotype.

The problem of causing unitypical and directed non-hereditary variations in animals and plants under experimental conditions, is an old subject for discussion and experiment.

In the present publication we should like to attract the attention of all concerned first to the general nature of the physiological discontinuance in ontogeny, and secondly, to the importance of a synchronous run of sensitive periods in a given population of organisms for production of directed non-hereditary variations in them.

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*GENETICS*

# ACTION OF X-RAYS AND HEAT SHOCKS ON DEVELOPMENTAL VARIATION IN *DROSOPHILA MELANOGASTER*

By M. E. LOBASHOV

*(Communicated by I. I. Schmalhausen, Member of the Academy, 21. IV. 1940)*

In the course of our studies on the influence of external factors on variation we came across the phenomenon of the dependence of heat shocks on other environmental factors affecting the physiological condition of the organism.

The study of the interaction of factors within the limits of the physiological optimum of the organism and beyond these limits (semi-lethal dosages) is of paramount importance for understanding the mechanism of the action of natural factors on mutation and developmental variation.

The purpose of the present work was to clear up the relation between the «power» of a heat shock in physiologically normal organisms and in the organisms affected with X-rays. As variation standard we used the frequency of occurrence of phenocopies of the mutation type «Notch» (notched wings). As test material two *Drosophila* populations «Samara» and «Bukhara» were used.

The larvae were irradiated before pupation (about 3000 r) and divided subsequently into two parts. One half was kept at low temperature (15—20°); the other half was shortly (2—4 hours) after X-ray treatment subjected to the action of a heat shock (35—36°) for 6 hours and was subsequently placed into the same temperature conditions with the first half of larvae. For the third set of experiments we used the data taken from some of the experiments (heat without irradiation) of V. I. Gratziansky, to whom thanks are due. His experiments were carried out almost simultaneously with ours and on the same kind of material. The experimental conditions are mentioned in the table.

Comparisons of the frequency of emergence of wing morphoses (notched wings) for irradiation alone, irradiation plus heat shock and heat shock without irradiation show that, if heat shock follows irradiation, this frequency is far greater than when each of these factors is acting singly. It is noteworthy that no simple summation of two effects is observed. However, the experiments with double application gave a higher frequency of morphoses amounting to $23.13 \pm 1.38$, which exceeds the expected frequency. A still more marked deviation from a simple summation of the cumulative effect produced when the two factors affecting development are acting in combination, is observed in the experiments with the line «Bukhara» which, as already noted, reacts more intensely to changing environmental conditions than does the «Samara» stock (3).

Action of X-rays and Temperature on the Frequency of Occurrence of Wing Morphoses (type of the *kn* effect) in *D. melanogaster* (X-ray dosage—about 3000 r; exposure to heat shock—6 hours)

| Line | Conditions of treatment | Temperature after exposure, °C | Total of flies examined for morphoses | Number of morphoses | % of morphoses |
|---|---|---|---|---|---|
| «Samara» | X-rays . . . . . | 15—20 | 1041 | 165 | 15.85±1.28 |
| | X-rays+35—36° . . . . . | 15—20 | 817 | 189 | 23.13±1.38 |
| | 35—36° (not X-rayed) . . | 24—28 | 1635 | 73 | 4.47±0.51 |
| «Bukhara» | X-rays . . . . . | 15—20 | 235 | 11 | 4.68±1.95 |
| | X-rays+35—36° . . . . . | 15—20 | 496 | 104 | 20.96±1.82 |
| | X-rays+35—36° . . . . . | 24—28 | 125 | 41 | 32.80±4.19 |
| | 35—36° (not X-rayed) . . | 24—28 | 1274 | 19 | 1.52±0.34 |

And it must be borne in mind also that in all the experiments when heat shock was applied singly, the exposure to heat treatment was four times that used when heat shock was combined with irradiation (see experimental conditions in the table). And this only went to increase the frequency of morphoses in the first case.

Another phenomenon connected with the frequency of occurrence of morphoses must be stressed. The per cent of perished larvae was not registered statistically after treatment; we have nevertheless noticed, that the higher the per cent of perished individuals after treatment, the greater the number of emerged morphoses.

It will be obvious that combined treatment (asynchronous) of *Drosophila* larvae with two semi-lethal dosages of factors affecting normal development of the organism results in so high a frequency of emergence of morphoses, as considerably exceeds that obtained by summing up the effects of each factor acting singly. Though this regularity was established for the variation of only one character, we are inclined to regard it as a general law underlying the action of external factors on the process of developmental variation and, possibly, mutation.

A heat shock is more effective in inducing variation in an organism affected by X-ray than in a «normal» organism. This conclusion might have been drawn a priori on account of the fact that a sick organism is always more susceptible to every kind of affection or injury than is a «healthy» one. This fact, although generally known, has not been taken into account, however, in analyzing the mechanism of the action of natural factors on the process of spontaneous variation. As a rule, unusual factors and contrasting conditions are sought for in order to explain spontaneous mutations. If all the above is taken into consideration, there will be no longer necessary to seek for unusual factors. As the power of the action of each factor on variation in the organism is a variable magnitude depending on the physiological condition of the organism, even a «feeble» factor may under certain conditions appear to be sufficiently powerful to call forth variation.

On the basis of our data concerning the action of heat shocks on variation, it is possible to assume that in nature a change of a single factor will sometimes suffice to alter the action of all the others which, without being changed directly, will become more powerful and show a progressively increasing effect.

The progressive increase in the rate of developmental variation under the influence of a succession of environmental factors is proved by one of our

experiments with «Bukhara» line. An insignificant change of developmental temperature after a treatment of larvae with X-rays plus heat shock proves to be an exclusively powerful factor in regulating the frequency of occurrence of morphoses (see table).

Although the material of our experiments is not sufficient for definite conclusions to be made, nevertheless our assumption as to the cumulative influence on the organism of asynchronously acting environmental factors which bring about an increase in variability, may be regarded as a general rule underlying the reaction of a developing organism to changes in its environment.

Finally, we wish to warn against an erroneous misinterpretation of our conclusions. We do not intend to assert that two factors responsible, if acting in combination, are found always to increase the variation effect. On the basis of the available physiological data on the interaction of two factors affecting the normal condition of the organism, the conclusion as to the progressive increase of affection is premature and even erroneous. Many instances are known when two different factors have a disturbing effect acting singly, no such effect at all when acting in combination; these are antagonistic factors.

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*ZOOLOGIE*

# EINIGE GESETZMÄSSIGKEITEN IN DER AUSNUTZUNG VON KOK-SAGHYZ DURCH INSEKTEN

Von M. S. GHILAROV

*(Vorgelegt von I. I. Schmalhausen, Mitglied der Akademie, den 22. IV. 1940)*

Bei der Untersuchung der Frage über die Schädigung des Kok-Saghyz (*Taraxacum kok-saghyz* Rod.) mit schädlichen Insekten wurde erkannt, dass diese neue Kulturpflanze in Plantagenbedingungen im europäischen Teil der UdSSR ausserordentlich gut von der einheimischen Entomofauna ausgenutzt werden kann. Die Wurzeln des Kok-Saghyz benagen in verschiedener Tiefe die Larven der auf den Feldern verbreiteten schädlichen *Scarabaeidae*, *Elateridae*, *Tenebrionidae* und *Alleculidae*. Einige Insektenarten fressen sich in die Hauptwurzel hinein (die Larven des Rüsselkäfers *Alophus triguttatus* Schr.), einige beschädigen hauptsächlich die dünnen Nebenwürzelchen (*Anisoplia segetum* Hbst., *Opatrum sabulosum* L.).

Die sich von Kok-Saghyz ernährenden Erdraupen (*Euxoa segetum* Schiff., *Feltia exclamationis* L.) beschädigen vor allem die obersten Teile der Wurzel (die Region des Wurzelhalses). Die Keimblätter und die ersten Blättchen des keimenden Kok-Saghyz fressen die Käfer *Tanymecus palliatus* F., *Opatrum sabulosum* L., verschiedene Arten der *Halticini*; die Blätter der etwas älteren Pflanzen fressen die Raupen des Wiesenzünslars (*Loxostege sticticalis* L.). Im Blattparenchym legen die Larven der Minierfliege (*Phytomyza* sp.) Gänge an.

Die Larven des Löwenzahnrüsselkäfers (*Ceuthorrhynchus punctiger* Gyll.) beissen, nachdem sie aus den Eiern, die in den Blütenständen abgelegt werden, geschlüpft sind, zu den sich entwickelnden Achänen steigend, Gänge in dem Blütenträger und dem Blütenboden. Aus den Blütenträgern und Hüllkelchen saugen verschiedene Wanzenarten (*Spilosthetus equestris* L., *Lygus pratense* L., *Codophila varia* F. u. a.) den Saft aus. Einige Käfer (*Mylabris* spp.) und Raupen (*Plusia gamma* L.) benagen die Blumenkronen, Staubbeutel und die Narben.

Den Blütenstaub des Kok-Saghyz nehmen die Vertreter der Gattung *Halictus* und andere wilde Bienen, den Nektar die Hausbiene (*Apis mellifera* L.), aber auch Hummeln (*Bombus*), Andrenen usw. Die sich entwickelnden und reifenden Achänen werden von den Larven der Fliegen (*Ensina sonchi* L., *Paroxyna tesselata* Loew., *Trypanaea stellata* Fuessly, *Gitona distigma* Meig.), von den Larven *Olibrus bicolor* F., den Rüsselkäferlarven *Ceuthorrhynchus punctiger* Gyll., den Raupen der *Heliothis dipsacea* L. und der *Acidalia rubiginata* Hufn. usw. gefressen. Einige Raupen fressen den Achänenpappus (*Cnephasia* sp., *Cacoecia costana* F.).

Die angeführte Liste enthält bei weitem nicht alle Insekten, die Kok-Saghyz als Nahrung ausnutzen können*.

Solch eine vollständige Ausnutzung einer neuen Pflanze, die erst seit kurzem kultiviert wurde, von den einheimischen Insekten (von denen viele oligophag sind), lässt sich grösstenteils dadurch erklären, dass die Entomocönose des Kok-Saghyz in der Hauptsache aus Insekten gebildet wird, die mit dem Kok-Saghyz nahestehenden Löwenzahnarten (*Taraxacum* spp.) in Verbindung stehen, d. h. Pflanzen, die schon längst von der autochtonen Fauna [vergl. (1)] ausgenutzt werden.

Zwischen den verschiedenen Insektenarten, die sich von denselben Pflanzen ernähren, entsteht ein Konkurrenzkampf. Günstig ist für die konkurrierenden Arten die Abschwächung des Zwischenartenkampfes, die durch die Ausnutzung verschiedener Pflanzenteile durch verschiedene Arten erreicht wird. Daher werden in den sich ausgebildeten gesättigten Biocönosen von den verschiedenen Tierarten verschiedene Teile der in sie eingehenden Pflanzen ausgenutzt (in unserem Falle des Löwezahns).

Der Drang, der Konkurrenz mit den anderen Arten zu entgehen, ist am klarsten unter den Vertretern solcher Gruppen der Insekten ausgesprochen, die sich vom Kok-Saghyz und anderen Löwenzahnpflanzen ernähren, und für die diese Pflanzen nicht nur die Nahrungsquelle, sondern auch das ständige Substrat, ein Lebensraum darstellen.

Die Verteilung verschiedener Pflanzenlausarten auf dem Kok-Saghyz (d. h. Insekten mit ähnlicher Ernährungsweise, wenig bewegliche und die im Laufe der ganzen Individualentwicklung die Nährpflanze nicht verlassen) kann als ein charakteristisches Beispiel dafür dienen, wie die Konkurrenz zwischen einzelnen Insektenarten vermieden (wahrscheinlich bedeutend abgeschwächt) wird, die sich auf kleinen Kräutern ansiedeln und sich von ihnen ernähren (siehe Tabelle).

Verteilung verschiedener Blattlausarten (*Aphididae*) auf dem Kok-Saghyz

| Blattlaus | Aufenthaltsort, an dem sich gewöhnlich die Pflanzenläuse auf dem Kok-Saghyz befinden |
|---|---|
| *Trifidaphis phaseoli* Pass. | An den dünnen Nebenwürzelchen, bis zu einer Tiefe von 30 cm |
| *Trama troglodytes* Heyd. | An der Hauptwurzel |
| *Xerophilaphis scorzonerae* Mordv. | In der Nähe des Wurzelhalses und in den Wunden des Hauptwurzels (ausgenagt von Ameisen *Lasius niger alienus* **) |
| *Aphis plantaginis* Schr. | An der Basis der Blätter und im Gebiet des Wurzelhalses |
| *Macrosiphum taraxaci* Kalt. | Auf den Blättern, hauptsächlich auf der Unterseite |
| *Aphis* sp. (schwarze Art)*** | Auf den jungen zentralen Blättchen und an der Basis der Blütenträger |
| *Macrosiphum sonchi* L. | An dem mittleren Teil der Blütenträger |
| *Myzodes persicae Sulz****. | Auf der Spitze der Blütenträger und an der Aussenseite des Hüllenkelchs |
| *Nasonovia ridicola* Kalt. | An der Innerseite des Hüllenkelchs |

* Es sind in der Hauptsache die Schädlinge, die in der Ukraine registriert wurden, angegeben.

** Ameisen verschiedener Art können die Wurzelblattläuse veranlassen ihren gewöhnlichen Aufenthaltsort zu ändern (2).

*** Diese Art ist nur für Gewächshäuser registriert worden.

Aus der Tabelle ist ersichtlich, dass sogar unter den Bedingungen einer gleichzeitigen Ernährung auf dem Kok-Saghyz die verschiedenen Blattlausarrten keine unmittelbare Wirkung aufeinander ausüben, wasdie Konkurrenz zwischen ihnen vermindert.

Nur in seltenen Fällen einer ausserordentlich starken Vermehrung der Blattläuse (z. B., in Gewächshausbedingungen in Michnewo, Moskauer Gebiet) wurde auf einzelnen Pflanzen, z. B., die Ausbreitung der schwarzen *Aphis* sp. nach oben den Blütenträger entlang auf dem Teile, der von *Myzodes* besetzt ist, beobachtet, während die hellgrünen *Myzodes* im Gegenteil die von *Aphis* eingenommenen Stellen besiedelten. In diesen seltenen Fällen wurden auf dem Kok-Saghyz Mosaik-Kolonien von Blattläusen beobachtet. Gewöhnlich haben die Kolonien dieser Blattläuse untereinander keinen Kontakt.

In einem gewissen Grade weichen auch die Larven verschiedener Insektenarten, die sich in den Blütenkörbchen des Kok-Saghyz entwickeln, dem Konkurrenzkampf aus. So entwickeln sich in den Samenkörbchen des zweijährigen Kok-Saghyz und anderer Löwenzahnpflanzen (z. B., *T. officinale*), die im Frühjahr und im Frühsommer blühen, die Larven von *Ceuthorrhynchus punctiger* Gyll. und *Olibrus bicolor* F. Die Entwicklung der Larven dieser Insekten verläuft in derselben Periode, wobei in demselben Blütenkorb nicht selten beide Schädlingsarten angetroffen werden.

Die Konkurrenz zwischen *O. bicolor* und *C. punctiger* wird dadurch abgeschwächt, dass die Larven der Rüsselkäfer sich von den Samenschalen der zentralen Ringe, die Larven der *O. bicolor* aber von den Samenschalen der äusseren Ringe ernähren. Dies kommt daher, dass die Käfer *C. punctiger*, die Eier im Blütenträger ablegen, und die aus dem Blütenträger nach oben kriechenden Larven gelangen zu den zentralen Samenschalen, die Larven des *O. bicolor* suchen grössere Samenschalen auf, welche sich gewöhnlich in dem äusseren Ring befinden (die Reifung der Blüten beginnt im Köpfchen von den Randgebieten aus).

In der entomologischen Literatur sind viele analoge Fälle bekannt, wo verschiedene schädliche Insektenarten, die sich von einer Pflanze ernähren,für die verschiedenen bestimmten Teile dieser Pflanze endemisch sind.

So ist, z. B., bekannt, dass verschiedene Borkenkäferarten verschiedene Teile der Bäume besiedeln ([3],[4]). Dasselbe ist auch für Cocciden bekannt. Verschiedene Rüsselkäferarten (*Ceuthorrhynchus*) entwickeln sich auf dem Senf, aber auf seinen verschiedenen Organen ([5]) usw.

Solch eine Differenzierung in der Auswahl der betroffenen Pflanzenteile zwischen den Insektenarten, die sich biologisch ähnlich sind (gewöhnlich auch systematisch mehr oder weniger nahestehen), wird nur in solchen Fällen beobachtet, wenn die Insekten in dem entsprechenden Stadium sich nicht nur von der Pflanze ernähren, sondern auch auf ihr wohnen, wenn die Pflanze ein mehr oder weniger ständiges Substrat der Insekten darstellt.

In den Fällen, wo solch eine enge Verbindung zwischen dem Insekt und der Nährpflanze nicht existiert, wenn das Insekt leicht von einer Pflanze zu einer anderen derselben Art übergehen kann, d. h. wenn die Pflanze nur die Nahrungsquelle für das Insekt darstellt, ist solch eine strenge Verteilung der ausnutzenden Pflanzenorgane unter den Vertretern jener oder anderen Schadinsektengruppe gewöhnlich nicht vorhanden.

Die beweglichen polyphage Käfer, z. B., ernähren sich auf den Blütenkörbchen des Kok-Saghyz und beschädigen sie gleichartig (*Zonabris crocata* Pall., *Lydus syriacus* L., *Lydus chalybaeus* Tausch., *Podonta daghestanica* Rtt., *Cteniopus sulphuraeus* L., *Omophlus proteus* Kitsch. usw.).

Verschiedene Arten der Drahtwürmer (Larven der *Elateridae*) beschädigen die Wurzel gleichzeitig, usw.

Dieselbe Lage wird auch in bezug auf die beweglichen Oligophagen beobachtet. Die Käfer verschiedener *Phyllotreta*-Arten, Schädlinge der Kreuzblütler, beschädigen gleichartig die Blätter, usw. Verschiedene Organe der Pflanze werden in den sich angebildeten gesättigten Biocönosen von Vertretern verschiedener biologischer Gruppen beweglicher Insekten beschädigt.

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*PHYSIOLOGIE*

# ÜBER DEN EINFLUSS DER TEMPERATUR AUF DIE ERREGBARKEIT DES GEHIRNS BEIM FROSCH

Von G. G. JAURE

*(Vorgelegt von P. P. Lasareff, Mitglied der Akademie, den 25. III. 1940)*

Bezüglich der Frage über das Entstehen der Krämpfe bei der Überhitzung des Gehirns, z. B. bei den Arbeiten an heissen Arbeitsstellen, ist in den Arbeiten von P. P. Lasareff theoretisch gezeigt worden, dass die Kurve der Erregbarkeit der Gehirnrinde ein Maximum haben muss. Auf beiden Seiten des Maximums, d. h. bei der Überhitzung wie auch bei der Abkühlung, erleiden die Zellen der Gehirnrinde eine Depression. Bei dieser Depression werden die Hemmungsimpulse auf die Unterrinde aufgehoben und die reflektorischen Akte werden stärker und breiter.

Diese Vorstellungen finden viele Bestätigungen in klinischen Vorfällen. Jedoch ist ein experimenteller Beweis an warmblütigen Tieren schwer zu erbringen, da es methodisch kompliziert ist nur den Einfluss der Temperatur zu erreichen, ohne dass gleichzeitig Veränderungen des Stoffwechsels vor sich gehen. Auf Grund dessen habe ich nach dem Vorschlag von P. P. Lasareff den Einfluss der Temperatur auf die Erregbarkeit der Gehirnrinde der kaltblütigen Tieren, und zwar am Frosch, untersucht.

Die Versuchsmethode war folgende. Dem Frosch wurde mit der Entfernung der Schädeldecke das Gehirn entblösst, danach wurde das Tier in einer ausgehöhlten Korkkammer, welche entsprechend der Grösse des Frosches verfertigt wurde, fixiert. Die Hinterbeine hingen frei aus dem ausgehölten Rand der Kammer. Das eine Bein brachte bei seiner Reaktion eine Feder des Myographen in Bewegung. An das entblösste Gehirn wurden zwei silberne nicht polarisierte Elektroden angeführt. Diese Elektroden waren durch den Kommutator mit einem Stöpselkondensator von einem Fassungsvermögen von 1 Mikrofarad verbunden. Der Kondensator wurde von einer Quelle gleichgerichtetem Strom mit einer Spannung von 30 Volt geladen. Die Entladungen des Kondensators dienten als Reiz für das Gehirn, und die Bewegung einer der Hinterpfötchen diente als Mass für die Erregbarkeit der motorischen Gebiete des Gehirns des Frosches. An den Kopf des Tieres wurde eine Pipette von 5 $cm^3$ angebracht. Die in diese Pipette aufgenommene Ringerlösung berieselte nach vorheriger Temperaturbestimmung das Froschgehirn. Sofort nach der Benetzung, d. h. sobald das Gehirn eine Temperatur, die der Temperatur der Lösung nahe war, annahm, wurde die Reizung des Gehirns mit Entladungen des Kondensators ausgeführt. In einer Zeitspanne von 5 Min. wurde eine neue Benetzung des Gehirns mit einer Lösung mit höherer Temperatur vorgenommen und wieder durch Entladungen gereizt. Der Unter-

schied der Temperatur zwischen zwei aufeinander folgenden Benetzungen war 2—3°. Nachdem die höchste Temperatur erreicht wurde (als solche hat sich aus einer grossen Anzahl von Beobachtungen eine Temperatur von 35° C gezeigt, höher verschwand die Erregbarkeit nicht reversibel), wurden die folgenden Benetzungen bei sinkender Temperatur ausgeführt. Einen vollen Zyklus von der niedrigsten Temperatur bis zur höchsten Temperatur und wieder zurück bis zur niedrigsten Temperatur auszuführen gelang uns nicht. Meistenteils war bei der Benetzung mit einer Temperatur der Ringerlösung von 30—32° schon die Erregbarkeit sehr gering und bei niedrigen Temperaturen verschwand sie vollständig.

Aus den erhaltenen Angaben über die Zusammenziehung der Pfötchen haben wir Kurven konstruiert, die die Erregbarkeit charakterisieren. An allen diesen Kurven ist zu ersehen, dass das Maximum zwischen 20 und 25° C liegt. Dieses Resultat ist auch an den Kimogrammen zu sehen. Da aber die einzelnen Amplituden der Reaktionen der Pfötchen auch bei gleicher Temperatur verschie-

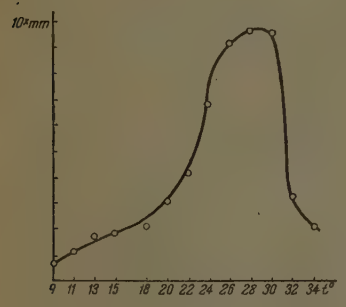


Abb. 1.

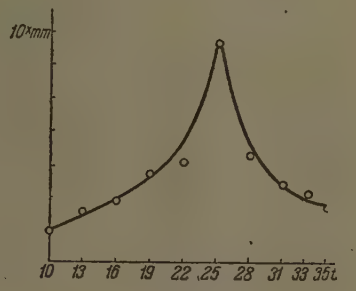


Abb. 2.

den sind, so haben wir bei der Aufstellung der Kurven dieselben im einzelnen gemessen und den Mittelwert für jeden Temperaturpunkt genommen. Dies erlaubte uns eine Tabelle und Kurve für jedes Kimogramm aufzustellen.

Tabelle 1 enthält die Angaben für einen der am besten gelungenen Versuche (in mm).

Tabelle 1

Mittelwert der Amplituden für Kimogramm No.5

| | | | |
|---|---|---|---|
| 9° — 0.7 | 15° — 1.8 | 22° — 4.1 | 28° — 9.6 |
| 11° — 1.1 | 18° — 2.0 | 24° — 6.8 | 30° — 9.5 |
| 13° — 1.7 | 20° — 3.4 | 26° — 9.1 | 32° — 3.2 |
| | | | 34° — 2.0 |

Tabelle 2

| | | |
|---|---|---|
| 10° — 0.9 | 19° — 2.67 | 28° — 3.25 |
| 13° — 1,57 | 22° — 2.95 | 31° — 2.38 |
| 16° — 1,86 | 25° — 6.66 | 33° — 2.15 |
| | | 35° — 1.65 |

Abb. 1 illustriert die Angaben dieses Versuches.

Um einen allgemeingültigen Schluss zu ziehen, wenn auch nur annährend, haben wir einige Kurven summiert und in einer Kurve dargestellt, welche die Gesetzmässigkeit in bezug auf den Einfluss der Temperatur auf die Erregbarkeit des Gehirns charakterisieren kann. In Tabelle 2 wird der Mittelwert der Amplituden der Zusammenziehung bei verschiedener Temperatur, welche die Resultate der Summierung aus einigen Versuchen darstellt, angeführt.

Die Kurve auf Abb. 2 illustriert die Angaben, welche in Tabelle 2 angeführt sind (in mm).

Die erhaltene Kurve fällt sehr nahe mit der Kurve, welche P. P. Lasareff theoretisch ausgeführt hat, zusammen. Andererseits, zeigt diese Kurve auch, dass das Maximum der Erregbarkeit des Gehirns des Frosches bei einer Temperatur von 25° C liegt.

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*MICROBIOLOGY*

# IDENTITY OF AGENTS RESPONSIBLE FOR THERMOPHILIC AND MESOPHILIC FERMENTATION IN CELLULOSE

By M. N. ROTMISTROV

*(Communicated by A. A. Richter, Member of the Academy, 4. V. 1940)*

Arousers of anaerobic fermentation in cellulose are a poorly investigated group of microorganisms. In the microbiological literature of to-day their generally adopted subdivision is into the mesophilic and the thermophilic ones. Omeliansky (1), Pringsheim (2, 3), Werner (4), Acharya (5), Simakova (6) and a number of other workers carried on the fermentation at temperatures ranging from 25 to 37° C. The range between 50 and 65° C was investigated by Mac Fayden and Blexall (7), Kroulik (8), Viljoen, Fred and Peterson (9), Woodman and Stewart (10), Veldhuis , Christensen and Fulmer (11), Pervozvansky and Cheltsova (12), Olson, Peterson and Sherrard (13). Bridging over the transition between these two intervals of temperature are the works by Khouvine (14, 15), who has isolated a pure culture of bacteria causing fermentation in cellulose at temperatures varying from 35 to 50° C. This pure culture appeared to combine the properties of both mesophilic and thermophilic bacteria. The temperature limits for the development and fermentation have not been studied in the majority of those works.

In our former experiments (16) we have found pure cultures of anaerobic cellulose bacteria to develop on potato agar at temperatures lying between 18 and 62° C.

From manure and soil samples we were able at 62—65° C to isolate more than fifty different cultures fermenting cellulose. All of them were enriched by boiling and passed five times on liquid media with cellulose at 62° C. From those elective cultures several pure ones were isolated by means of an original method. Four of them have been used in the experiments described in this paper. Cultures Nos. 21 and 27, isolated from a single cell; Nos. 24 and 39 purified on agar plates by five times repeated passages; Nos. 21 and 27 had sustained several tens of passages at 62° C and already used in our works on thermophilic fermentation of cellulose (17, 18).

Preliminary experiments with these thermophilic bacteria showed them to cause fermentation in cellulose at 62, 50 and 40° C. This being established, the cultures were used in our attempt to clear up the question as to whether the agents causing thermophilic fermentation in cellulose are or are not different from those responsible for its mesophilic fermentation. The experiments were arranged as follows.

Fermentation was carried on in round flascs, each of 250 $cm^3$ capacity. Our medium was the following composition: superphosphate, 5 g; $NH_4Cl$,3 g; KCl, 1 g; tap water, 1 l. This medium contained 3% of filter paper. The acid products of fermentation were neutralized with chalk. Analysis of culture media after fermentation was made according to the usual methods described in our previous papers ([17], [18]). The results of all experiments are expressed in grams per liter of medium and in per cent of fermented cellulose.

In Table 1 are summarized the experimental data on fermenting cellulose with pure culture No. 21 at various temperatures.

| Fermentation temperature | % of cellulose in medium | Fermentation length in days | % of fermented cellulose | Found in the medium | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Alcohol | | Formic acid | | Acetic acid | | Butyric acid | | Lactic acid | | Total product | |
| | | | | g/l | % | g/l | % | g/l | % | g/l | % | g/l | % | g/l | % |
| 62° | 3 | 10 | 79.0 | 1.08 | 4.7 | 0.44 | 1.9 | 8.0 | 35.5 | 5.2 | 23.1 | 0.36 | 1.6 | 15.08 | 66.9 |
| | | | 85.8 | 1.08 | 4.4 | 0.42 | 1.8 | 7.28 | 30.0 | 4,8 | 19.6 | 0.28 | 1.1 | 13.86 | 56.9 |
| 45° | 1.5 | 30 | 90.2 | 0,05 | 0.4 | 0.69 | 5.1 | 4.77 | 35.3 | 1.61 | 11.9 | 2.08 | 15.4 | 9.2 | 68.1 |
| | | | 93.7 | 0.02 | 0.1 | 0.14 | 1.1 | 4.97 | 37.4 | 1.35 | 10.2 | 1.71 | 12.9 | 8.19 | 61.7 |
| 35° | 3 | 174 | 44.1 | 0.05 | 0.4 | none | — | 0.13 | 1.0 | 1.14 | 9.2 | 2.20 | 17.6 | 3.52 | 28.2 |
| | | | 71.5 | 0.07 | 0.5 | 0.74 | 3.6 | 0.36 | 1.8 | 2.46 | 12,1 | 2.14 | 10.5 | 5.77 | 28.5 |

It is seen from the table, that the fermentation lasted longer when the temperature was lower. But there was no such regular variation in the per cent of fermented cellulose. If the latter was higher at 45° C, it was merely because less cellulose was available in the medium. The same products were always found in the media whatever the temperature of fermentation might have been.

No regularity could be detected in the storage of formic acid. But the alcohol showed a definite tendency to decrease in amount with decreasing temperature and increasing length of fermentation. So, too, did the acetic and butyric acids, while the lactic acid furnished a directly opposite instance. The total product of fermentation in the medium decreased with temperature. All at the same time when the temperature was low enough, an intensive formation of gases was taking place,

Why the yield of total product should be lower at 45 and 35° C may be explained in terms of two factors. The first is that biochemical reactions are shifted to make for a more intense gas formation; the second is the consumption of fermentation products by bacteria in the run of a long contact (well increased interval of fermentation). It is in this way that at 35 and 45° C the same products are formed as at 62° C, but in lesser quantities. The per cent of fermented cellulose remains mainly invariable through all these three temperatures. Only the length of fermentation is liable to change. The data tabulated hereafter refer to fermentation of cellulose on the same medium deprived of organic nitrogen, caused by various pure cultures of thermophilic bacteria. The medium contained 3% of cellulose; fermentation temperature, 35° C (Table 2).

Table 2

| Nos. of cultures | Fermentation length in days | % of fermented cellulose | Found in the medium | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Alcohol | | Formic acid | | Acetic acid | | Butyric acid | | Lactic acid | |
| | | | g/l | % | g/l | % | g/l | % | g/l | % | g/l | % |
| 24 | 186 | 62.3 | 0.46 | 2.6 | 0.26 | 1.4 | 2.7 | 15.3 | 0.23 | 1.3 | 1.82 | 14.4 |
| 27 | 120 | 90.3 | 1.12 | 4.3 | 0.58 | 2.2 | 8.9 | 34.6 | none | — | 3.05 | 11.9 |
| 39 | 190 | 69.5 | 0.05 | 0.2 | 0.22 | 1.1 | 0.87 | 4.4 | 2.07 | 10.5 | 2.04 | 10.3 |

From these data it is evident that at 35° C the fermentation was slow with all the three cultures; but at the end of the process no less than 60% of the cellulose had been fermented. In the case of culture No. 27 the fermentation was sooner complete. It took 120 days as against more than 6 months, which was the case with cultures Nos. 24 and 39. Under similar conditions but with 62° C these cultures brought fermentation to an end in 8—10 days. The fermentation products were the same with 35° as with 62°. But their amounts were not the same. Less acetic acid, butyric acid and alcohol was yielded at 35° C, and more lactic acid.

If the data in Tables 1 and 2 be compared with those reported by Omeliansky (1), we shall find them all to have a great deal in common.

To verify whether pure cultures of thermophilic cellulose bacteria are able to produce fermentation in cellulose under the conditions available in Omeliansky's experiments, we inoculated his media with cultures Nos. 21 and 27, isolated by means of a micromanipulator from a single cell. The media contained 1.5% of cellulose; temperature, 35° C. Neutralization, with chalk. The results are summarized in Table 3.

Table 3

| Nos. of cultures | % of fermented cellulose | Found in the medium | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Alcohol | | Formic acid | | Acetic acid | | Butyric acid | | Lactic acid | |
| | | g/l | % | g/l | % | g/l | % | g/l | % | g/l | % |
| 21 | 51.6 | 0.3 | 4.1 | 1.31 | 17.8 | 1.76 | 23.9 | 0.32 | 4.3 | 2.15 | 29.3 |
| 27 | 76.9 | 0.19 | 1.7 | 0.59 | 5.4 | 1.82 | 16.6 | 1.24 | 11.3 | 1.47 | 13.5 |
| | 67.4 | 0.14 | 1.4 | 0.10 | 1.0 | none | — | 1.88 | 19.6 | 1.29 | 13.5 |

The fermentation in these experiments, in which its conditions were reproduced exactly as they had been set up by Omeliansky, presented a picture quite identical with that described for mesophilic bacteria. Hence a single kind of bacteria is able to cause now a thermophilic and now a mesophilic fermentation in cellulose. Pure cultures isolated at 62° C and gone through many passages on cellulose at that temperature, perfectly fermented the cellulose at 45 and 35° C.

From these and a number of similar experiments not described here we have come to the conclusion that there is no good reason for dividing the

anaerobic cellulose bacteria into thermophilic and mesophilic ones. We are only entitled to speak of a thermophilic or a mesophilic fermentation in cellulose, which both are probably due to a single kind of bacteria.

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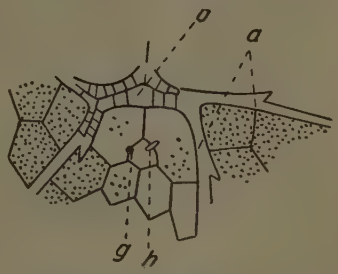
*PALÉONTOLOGIE*

# SUR LES PORES PRIMAIRES DE *PROTOCRINITES* ET D'AUTRES CYSTIDÉS

Par N. YAKOVLEV, membre correspondant de l'Académie

En déterminant des fossiles récoltés en été 1939 sur les bords de la rivière Volkhov par les participants à une excursion scolaire, j'ai remarqué un échantillon de *Protocrinites fragum* qui, quoique brisé des deux cotés opposés, conservait des pores primaires plus nets que ce n'est ordinairement le cas schez les cystidés en général.

Dans son ouvrage capital «Stammesgeschichte der Pelmatozoen» ([1], p. 363), Iaekel dit à propos des pores primaires—gonopore et hydropore (madréporite)—qu'il n'a pu trouver de madréporite chez les *Protocrinites* russes, tandis qu'il l'a bien observé chez leurs représentants isolés de Bohème. Il convient de remarquer que le représentant bohémien de *Protocrinites — P. rarissimus*, à juger d'après la figure donnée par Iaekel (pl. III, fig. 9), laisse à désirer comme conservation, les limites entre les plaques du calice n'y sont pas visibles et il n'est par conséquent pas possible de dire sur quelles plaques exactement sont situés l'hydropore (Pr) et le gonopore (Pp).




Structure de l'aire orale de *Protocrinites fragum*. *o*—orifice oral, recouvert par les plaques ambulacraires; *a*—sillons ambulacraires; *g*—gonopore; *h*—hydropore.

Notre exemplaire de *P. fragum* permet de le dire. En effet, la partie supérieure de l'interradius anal y est formée, comme d'ordinaire, de trois plaques disposées en une rangée horizontale, la médiane étant de moindre dimension que les deux autres et même plus petite que ce n'est généralement le cas. Les pores primaires sont situés à la limite des plaques contigües à la médiane, celui de droite devant être l'hydropore et celui de gauche le gonopore, par analogie avec les autres cystidés.

J'ai donné ailleurs ([2]) les caractères corrigés des pores primaires et leur rapport aux plaques du calice chez *Chirocrinus*, *Echinoencrinus* et *Cystoblastus*. Pour *Chirocrinus* Iaekel ne fournit aucune indication sur la disposition des pores primaires; chez *Echinoencrinus* il n'a été en mesure de les discerner qu'après le polissage, qui n'a toutefois pas montré les interrelations précises; pour *Cystoblastus* il se borne à reproduire la figure de Volborth (dont l'original est perdu), où le madréporite est indiqué inexactement.

Ainsi que je l'ai signalé et figuré, les pores primaires et leur disposition sont semblables chez ces trois genres. Ils se trouvent chez tous les trois au sommet de l'interradius anal, sur trois plaques, comme chez *Protocrinites*, l'hydropore et le gonopore de *Chirocrinus* et d'*Echinoencrinus* étant situés à la limite entre la plaque médiane et celle de gauche, l'hydropore au-dessus du gonopore, tandis que chez *Cystoblastus* l'hydropore, qui représente un assez grand espace perforé en tamis, reste en contact aussi avec la plaque de droite, ce qui peut être considéré comme une particularité commune à *Protocrinites* et *Cystoblastus*.

Nous constatons une disposition des pores primaires identique à celle de *Chirocrinus* et *Echinoencrinus* chez *Pleurocystis* (Iaekel, fig. 30 A, p. 131) et identique à celle de *Protocrinites* chez *Glyptosphaerites* (Iaekel, pl. IV, fig. 4). Iaekel (p. 139) subdivise les cystidés en trois groupes sous le rapport du gonopore: 1) à gonopore situé sous le madréporite, 2) à gonopore et madréporite confondus, 3) à gonopore atrophié. Les deux derniers groupes sont peut-être malaisés à distinguer entre eux; mais ce qui importe surtout, c'est d'y ajouter un groupe à madréporite et gonopore disposés (non l'un au-dessus de l'autre, mais l'un à côté de l'autre) sur les deux sutures de la plaque moyenne avec les plaques de droite et de gauche.

Si, avec Iaekel, on considère *Cystoidea Dichoporita* comme dérivant de *Diploporita*, la disposition des pores primaires l'un à côté de l'autre dans le sens horizontal, ainsi que chez *Protocrinites*, devra être regardée comme primaire, et leur disposition verticalement l'un au-dessus de l'autre, telle qu'on la constate chez *Chirocrinus* et d'autres cystidés, comme secondaire. En établissant ces deux groupes, il s'agit de savoir comment concilier l'existence du second groupe et la disposition des pores primaires dans la cloison pariétale verticale, relation présumée par Iaekel.

Nous n'avons examiné que les cystidés qui ne soulèvent aucun doute quant aux particularités de l'hydropore et du gonopore.

Institut Géologique de l'URSS.
Leningrad.

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*PALEONTOLOGY*

# THE FIRST REPRESENTATIVE OF THE GENUS *BISATOCERAS* FROM THE UPPER PALEOZOIC OF THE URALS

By S. V. MAXIMOVA

*(Communicated by A. A. Borissiak, Member of the Academy. 29. V. 1940)*

Representatives of the genus *Bisatoceras* have so far been known only from the Middle Carboniferous of the United States: *B. primum* from the Coffeyville formation, Oklahoma, and *B. greenei* from the Cherokee series, Missouri. The Cherokee series lies at the bottom of the Middle Carboniferous, the Coffeyville formation occupies a higher position, but still within $C_2$. My collection from the Schwagerina beds of Yurezan river ($P_1$) contains a species, all the main characters of which make it referable to this ancient genus.

In 1937, A. K. Miller and J. B. Owen erected a new genus, *Bisatoceras*, which has the following characteristic: conch subdiscoidal, laterally compressed, with closed umbilicus. The sculpture is composed exclusively by transverse striae forming sinuses on the flanks and venter and salients near the umbilicus and in the region of the ventral shoulder. The suture forms a total of 8 lobes. The branches of the ventral lobe are very broad, the ventral saddle being almost as high as the external one. The lateral lobe is acuminate, the umbilical lobe short, rounded. The internal lobe is quite narrow, acuminate, the dorsal lobe fairly narrow, linguiform. This genus was represented by a single species, *B. primum*.

In 1938, Miller and Moore described a new species, *B. secundum*, and in 1939, Miller and Owen erected one more species, *B. greenei*. The latter is similar in all characters to the genotype, and is in full agreement with the above generic diagnosis. On the contrary, *Bisatoceras secundum* possessing many features in common with the genotype, differs distinctly from the latter in its sculpture. The conch of this form is marked by numerous distinct longitudinal ribs of the *Agathiceras* type. Further the conch of this species is markedly broader than that of *B. primum* and *B. greenei*. In the two latter the longitudinal ribs are completely lacking, and the sculpture consists merely of transverse striae which are so pronounced that may be discernible even in cast (see Miller and Owen, 1937, pl. 50, figs. 6—7, and the same authors, 1939, p. 155). Generally, in the shape of the conch and the sculpture *Bisatoceras primum* and *B. greenei* show a very close resemblance to *Prothalassoceras* and *Thalassoceras*, while *Bisatoceras secundum* is very much suggestive in the same characters of *Agathiceras*. Since the sculpture is an essential and inseparable generic character, I suggest that *Bisatoceras secundum* be separated as a new genus, *Pseudobisatoceras*, with *P. secundum* (Miller and Moore) as the type species.

The suture-line of *Bisatoceras* is very peculiar and characteristic. The ventral saddle is very high, almost as high as the external saddle. The branches of the ventral lobe are very broad, with almost straight and parallel sides, and with a small and short papillary point at the base. They are either as broad as the lateral lobe or broader. The lateral lobe is nearly bell-shaped, slightly asymmetrical, tapering towards the base, with no constriction at the top. The lateral saddle is low, quite broad, asymmetrical. The umbilical lobe is short, rounded or cuneiform. The internal lobe is subcuneiform, very narrow, linguiform, or lanceolate. It is $^1/_2$—$^3/_4$ as broad as the lateral lobe. A characteristic feature of the internal suture is the close

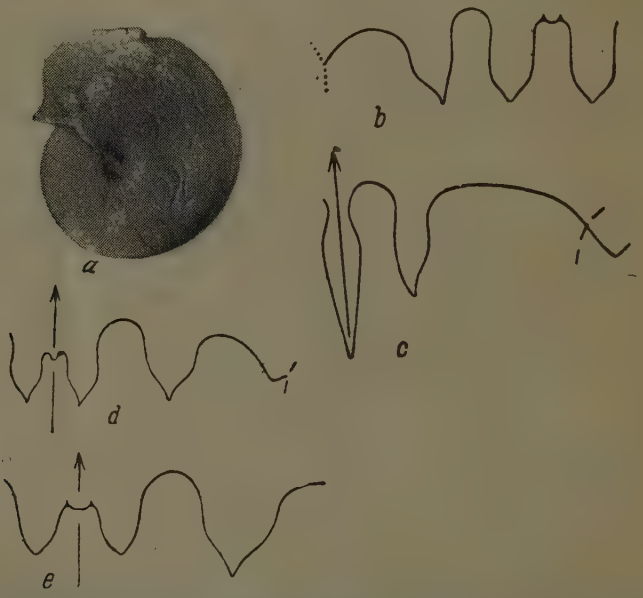


Fig. 1. *Bisatoceras satrum* sp. nov.: *a*—holotype (×1); *b*—external lobular line of the same specimen with $H=14$ mm (×2); *c*—internal lobular line with $H=20$ mm (×2.5); *d*—lobular line with $H=8$ mm (×3); *e*—lobular line of the young form with $H=2.5$ mm (×10).

spacing of all the lobes in the centre of the whorl, so that between the umbilical seam and the internal lobe a very wide space is left occupied by a low, very broad, asymmetrical second internal saddle. In shape this saddle is very much like the lateral saddle.

Measurements of the specimen No. 1 have been taken in the very beginning of the living chamber. Its full diameter is 50 mm.

*Bisatoceras satrum* sp. nov.

Dimensions in mm

| Specimen | *D* | *H* | *W* | *U* | *H* : *D* | *H* : *W* | *U* : *D* |
|---|---|---|---|---|---|---|---|
| I | 35.4 | 21.0 | 21.5 | 0 | 0.62 | 0.97 | — |
| II | 10.9 | 7.5 | 8.0 | 0 | 0.70 | 0.94 | — |

The conch at the adult stage is subdiscoidal (thickly discoidal). The whorl section is elliptical. The ventral shoulder is gently rounded. The umbilical shoulder is rather narrowly rounded. The height of volution is equal to 0.97 of its width. The ultimate volution embraces entirely the preceding one. Umbilicus closed.

Not a single specimen has the conch preserved. The cast is perfectly smooth.

The preserved portion of the living chamber is one volution in length.

On the length between $D=10.9$ mm and $D=35.4$ mm the shape of the conch remains almost unchanged, and only the height ratio ($H : W$) is slightly increased.

At $H=20$ mm the external suture forms the ventral, one lateral and one umbilical lobes. The ventral lobe is divided by a very high ventral saddle into two branches. The height of the ventral saddle is $^9/_{10}$ that of the ventral lobe. The branches of the ventral lobe are very broad with almost straight and parallel sides, and with a small, short papillary point at the base. The lateral lobe is subcuneiform, slightly asymmetrical, gradually tapering towards the base, with no constriction at the top. The lateral lobe is slightly narrower than either branch of the ventral lobe. The lateral saddle is low, quite broad, asymmetrical. The umbilical lobe is short, cuneiform.

At $H=20$ mm the internal suture forms the dorsal and one internal lobes, and two saddles. The second internal saddle (closest to the umbilicus) is low, very broad, asymmetrical, and is very much like in shape the lateral saddle. The internal lobe is narrow, long, nearly cuneiform. It attains $^3/_4$ of the length of the dorsal lobe. The latter is long, very narrow, lanceolate. A maximum width it attains at about $^1/_4$ of its height (in descending direction). Beginning with this portion the lobe gradually tapers towards the base. The dorsal lobe is approximately $^1/_2$ as wide as the lateral one. All lobes of the internal suture are very closely spaced in the centre of the volution.

At $W=6$ mm the ventral saddle attains only a half of the height of the ventral lobe. The branches of the ventral lobe are linguiform, narrow. The lateral lobe is bell-shaped, broad. It is $1^1/_2$ as broad as either branch of the ventral lobe. Its base is markedly lower in position than that of the ventral lobe. The lateral saddle is asymmetrical, broad. At $W=8$ mm the ventral saddle attains already $^3/_4$ of the height of the ventral lobe. The branches of the latter assume outlines characteristic of those at the adult stage, but still remain markedly narrower than the lateral lobe. The lateral lobe is the same as at $W=6$ mm.

The species under consideration differs from *Bisatoceras primum* and *B. greenei* in the broader volutions and the narrower branches of the ventral lobe. Indeed, in both mentioned species volutions are more high than broad, whereas in *B. satrum* they are slightly broader than high. In the American species the branches of the ventral lobe are about $1^1/_2$ as broad as the lateral lobes, whereas in *B. satrum* the branches of the ventral lobe are almost as broad as the lateral lobe.

Locality: outcrop 2 km north-east of Akhunovo, Mount Satra. Lower part of the Schwagerina beds.

Holotype: specimen No. 1.

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*PALEONTOLOGY*

# *JURESANITES*, A NEW GENUS OF THE FAMILY *SOMOHOLITIDAE*

By S. V. MAXIMOVA

*(Communicated by A. A. Borissiak, Member of the Academy, 29. V. 1940)*

In 1938, I brought home from the Yurezan river a rather large and diversified collection of ammonoids of the lower part of the Schwagerina beds (base of the Sakmarian). In it a peculiar primitive twelve-lobed form was discovered which I describe here under a new generic name, *Juresanites*.

The conch consists of slowly increasing, low, broad, arched whorls. Umbilicus wide, attaining almost half of the diameter of conch, nearly conical. No tubercles on the umbilical shoulder. Sculpture fine, reticular. Constrictions form on the ventral side of the conch a broad salient. Ventral lobe divided by a ventral saddle into 2 branches basally pointed. Each of them is about ½ as wide as the first lateral lobe. The latter is bulbiform, constricted at the top, expanded in the middle, with a long point at the base. Second lateral lobe incipient. Umbilical lobe long, narrow, cuneiform, located just inside the umbilical shoulder. Dorsal lobe wide, bulbiform, constricted at the top, markedly expanded in the middle, with a long point at the base. It is only slightly narrower than the first lateral lobe. First internal lobe is constricted at the top, expanded in the middle, with a long point at the base. The second internal lobe is incipient.

Type species: *Juresanites primitivus* sp. nov.

*Juresanites* closely resembles *Somoholites* Ruzh. in the form of the conch and the outlines of the suture-line, but differs from the latter in having an additional pair of lobes. It differs from *Metalegoceras* Schind. in its primitive suture-line, outlines of the latter, and, apparently, different phylogenetic origin. Indeed, in *J. primitivus* (genotype) at $H=11$ mm the additional pair of lobes appears as simple projections on the saddle sides, while in the oldest member of the genus *Metalegoceras* (*M. distale* Ruzh., from the upper part of the Schwagerina beds) these lobes have this form at $H=2.8$ mm, and in the Artinskian *M. razumovskajae* Voin. at $H=1.5$ mm. The new character develops in *J. primitivus* very late: at $H=$approximately 4.5 mm there are no indications of the additional lobes.

The following consideration speaks in favour of the lines of descent of *Juresanites* and *Metalegoceras* being different. *Metalegoceras* descends from *Eoasianites*, and prior to the development of the additional lobes passes the *Eoasianites* stage. At this stage it has a total of 8 lobes, the lateral ones being linguiform, relatively narrow (only 1½ as wide as each branch of the ventral lobe), much shorter than the ventral lobe (i. e. the suture-line is quite like that of *Eoasianites*). *Juresanites* at early stages has also a total of 8 lobes,

but their relations are quite different. The lateral lobe is markedly longer than the ventral one, very wide (nearly 3 times as wide as each branch of the ventral lobe), expanded in the upper part. The relations of the lobes in the 8-lobed forms are very constant, and therefore they are of an important character. Indeed, in all species of *Eoasianites*, in all species of *Metalegoceras*

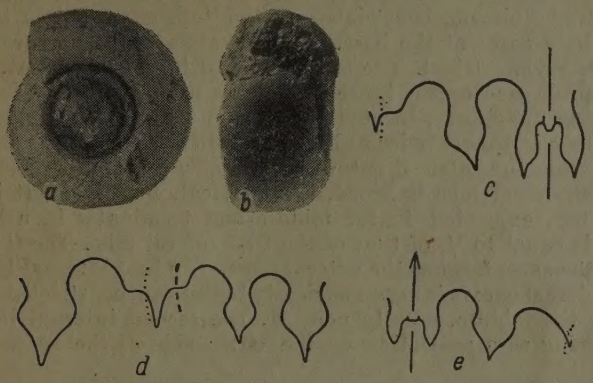


Fig. 1. *Juresanites primitivus* gen. et sp. nov.; *a* — *b* — holotype (× 1); *c* — external lobular line of the holotype with $H = 8$ mm (× 2); *d* — internal lobular line of the holotype with $H$=11 mm (×3); *e* — lobular line of a young specimen with $H$=about 4.5 mm (×3.5).

and *Riphaeites* (descendants of *Eoasianites*), at early stages the lateral lobe is short. In *Juresanites*, at the early stage the relations of the lobes are different, which indicates that its ancestor was not *Eoasianites*, but some other form.

*Juresanites primitivus* sp. nov.

Dimensions in mm

| | |
|---|---|
| $D$ — 31.5 | $H : D$ — 0.36 |
| $H$ — 11.5 ? | $H : W$ — 0.60 |
| $W$ — 19.5 | $U : D$ — 0.47 |
| $U$ — 15.0 | $W : D$ — 0.62 |

Volutions low, broad, arched. Width of volution equals approximately 0.62 of the diameter of the conch, and is 1.7 times as great as the height of volution. The ventral border is not formed. Umbilical shoulder narrowly rounded.

Umbilicus broad, attaining almost ½ the diameter of the conch, nearly conical. The volution embraces the preceding one so that in the umbilicus only a narrow band along the umbilical shoulder is left visible. Umbilical walls steep.

Sculpture reticular. It consists of numerous fine longitudinal striae and of equally numerous fine transverse striae. Both systems of striae are equally well pronounced. The transverse striae form a sinus on the outer surface of the conch; near the umbilical wall the transverse striae are arranged directly transversely to the surface of the wall. The cast is entirely smooth.

The constrictions on the outer surface of the volution form a sinus near the umbilical shoulder, and thereafter a salient.

At $H$=11 mm the external suture forms a broad ventral lobe, two lateral and one umbilical lobes. The ventral lobe is divided by a high bottle-shaped ventral saddle into two branches, the saddle attaining approxima-

tely half the height of the external saddle. The branches of the ventral lobe are asymmetrical, constricted at the top, expanded in the middle, with a long and narrow point at the base. The outer side of these branches is more convex than the inner one. The ventral saddle is broader than either branch of the ventral lobe. The external saddle is somewhat asymmetrical, rounded at the top, and constricted in the middle. The first lateral lobe is somewhat asymmetrical, bulbiform, constricted at the top, expanded in the middle, and with a long point at the base. The lateral saddle is narrower than the external one, asymmetrical. The second lateral lobe is incipient, appearing as a simple projection on the inner side of the lateral saddle. The umbilical lobe is narrow, cuneiform, located just inside the umbilical shoulder. The first lateral lobe is almost twice as broad as either branch of the ventral lobe.

At $H=11$ mm the internal suture consits of a dorsal lobe and two internal ones. The dorsal lobe is broad, symmetrical, bulbiform; it is constricted at the top, expanded in the middle and terminates in a long point. In width it is equal to $^3/_4$ of that of the first lateral lobe. The first internal saddle is of the same form as the external one. The first internal lobe is $^3/_4$ as broad as the dorsal one; it is asymmetrically bulbiform, constricted at the top, expanded in the middle, basally pointed. The second internal lobe is incipient, appearing as a projection on the outer side of the second external saddle.

At $H$=about 4.5 mm the external suture-line consists of a ventral lobe and one lateral on either side of it. Ventral lobe relatively narrow (only slightly wider than the lateral lobe). Branches of the ventral lobe narrow, lanceolate, with no point at the base. External saddle high, rounded at the top, constricted in the middle. Lateral lobe very wide, expanded in the middle, terminating in a narrow point. It is nearly three times as wide as each branch of the ventral lobe. Its base is distinctly lower than the base of the ventral lobe. Lateral saddle wide, asymmetrical. Umbilical lobe narrow, cuneiform, disposed just inside the umbilical shoulder.

*Juresanites primitivus* is at present the only representative of the new genus, thus no comparison with other species is needed.

L o c a l i t y: left bank of the Yurezan, below the mouth of the Uskandy. Lower part of the Schwagerina beds.

H o l o t y p e: a complete specimen.

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